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MULL AND DUFF[1] AS BIOTIC EQUILIBRIA

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The father of modern forest soil science, P. E. Müller, looked upon the humus layer in the forest as a biological unit. He regarded the strikingly different forms which it assumes in nature as immediately caused by corresponding differences in the visible or invisible "microcosm" composing the living part of the humus layer. The more recent developments in the field seem to indicate a distinct change in attitude, a trend leading away from Müller's biological viewpoint, approaching in many respects the chemical conception favored by the Liebig period. Today the biological characteristics are mostly regarded as merely indicative of the different types, as conditioned rather than conditioning (53, p. 525–526). The responsible factors are sought largely in chemical variations, either primary or secondary (climatic), of the mineral soil or of the organic materials that are undergoing decomposition.

Two things, in particular, seem to account for the decreasing weight given to Müller's biological ideas and for the emphasis again being placed on chemical considerations. One is the attitude of the leading German authority, Ramann. Although he was aware of the importance of biological factors, Ramann does not seem to have been in sympathy with Müller's unitary outlook. He preferred to study single aspects rather than the biological complex as a whole, just as in classification he chose to deal with the isolated components of the humus layer rather than with the humus layer itself (52, pp. 569, 573). It is probably due to Ramann's influence that even Müller's fundamental notion of the *humus layer* has not been much used outside of Scandinavia. Another, and probably the most important, factor which has contributed to the disregard of Müller's ideas is the overwhelming influence of the brilliantly developing regional soil science. As a result, the biological factors, including the higher vegetation, have come to be regarded more or less as merely tools of climate in determining or modifying soil conditions (52, p. 569–570).

The modern views characterized in the foregoing are shared even by workers who have approached the field as biologists. For instance, Hesselman considers the influence of the vegetation as an indirect effect of the climate (19, p. 205, 516). He explains the rôle of the tree species in influencing the type of humus layer on the basis of chemical differences of the

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[1] The terms employed in the present paper ("humus layer," "mull," "duff," etc.) have been defined previously (52). "Duff" has been retained as a term to cover P. E. Müller's "Mor" type of humus layer, although this proposal has met with some opposition on the ground that the word has been used and is being used in other senses. The writer, although feeling this criticism to be perfectly justified, has chosen to retain the term for the present, because all his efforts have failed to obtain an agreement on some other term. If "duff" cannot finally be agreed on by a sufficiently representative majority, the writer would propose for consideration the word "sweard," (the old Anglo-saxon form of the modern "sward"). This root, common to the teutonic languages, and meaning a pelt or hide either on a pig, etc., or on the ground, would seem particularly fit to cover the notion, and in the form "sweard" it would at the present time be absolutely distinctive.

[2] The laboratory work involved in the present study, and much of the field work in the four type localities, has been done by Mr. G. Cavetz. Some of the sampling in the field (soil and plants) was done by Mr. C. Heimburger. To both, the author's thanks are due.

litter. He regards the different development of the humus layer, starting from the same primary material, as essentially due to a different rate of decomposition which is partly governed by and partly governing the balance between the supply of bases and their loss due to leaching (19, p. 357–365, 531–538).

In the present paper, some facts (partly new, but mostly collected from the literature) will be brought together which seem to indicate that the chemical viewpoint current today, useful as it is, is somewhat onesided. Moreover, it will be shown that a number of empirical data can be more easily explained biologically and from the general standpoint held by P. E. Müller.

Parts 2 and 3 of the paper will appear in a later issue. In part 2, an effort will be made to indicate the biological differences between humus layers of different type and to suggest their significance. In part 3, the silviculturally important question of the effects of various disturbances will be treated from what is believed to be somewhat new points of view.

I. TYPE VERSUS RATE OF DECOMPOSITION

Historical

In P. E. Müller's "Studies," a different *rate* of decomposition is barely mentioned (38, p. 70; 40, p. 57) in his discussions of the differences between the mull and the duff type of humus layer. It is true that Müller has several statements regarding an apparently extremely slow decomposition in the duff, but these refer very specifically to certain brownish fungous mycelia, and not to the duff as a whole, nor to its decomposing plant residue in general. Only in one place (38, p. 35; 40, p. 30) is the statement made that this "almost indestructible" fungous mycelium "imparts some of its resistance to the duff." Instead, Müller lays the stress on the different mode or *type* of decomposition (38, p. 8, 17, 43, 45, 68, 70, 72, 81; 39, p. 78, 147, 155, 159–160, 162; 40, p. 8–9, 15, 36, 37, 55, 56, 58, 65, 178, 234, 240, 243, 245). This attitude is based on extensive and careful observation, as is usual in Müller's work. It is not accounted for by the fact that he shared the common, mistaken (50) view of a poor aeration being generally characteristic of the duff. In fact, his lack of emphasis on the rate of decomposition, as a distinctive difference between mull and duff, is in a way in peculiar contrast to his conception of duff formation as a more or less anaerobic process, altogether parallel to peat formation (he even called the duff "Torf" in the German edition of his studies).

Ramann, the leading authority in the later development, from the first stressed the rate of decomposition as a fundamental difference between mull and duff. The best forest soils, he said, are poor in humus, because of the rapid decay (46, p. 349–350; 47, p. 153; 48, p. 169). He ascribed duff formation to a slow decomposition (46, p. 177–179, 198, 201, 220; 47, p. 92–93, 131; 48, p. 463, 467). Yet, in the first edition of his textbook, Ramann assumed a difference between mull and duff, also in the type of the decomposing processes. A duff results, he said, "when conditions are unfavorable to decay and putrefaction predominates" (46, p. 231). In the following editions, the last three words have been cancelled (47, p. 159; 48, p. 193). Ramann evidently favored the idea of differences in the mode of decomposition only as long as he believed that they corresponded to Liebig's distinction between decay and putrefaction.

When he abandoned this view (48, p. 148), a different rate of decay remained as the essential difference between mull and duff formation.

Today the rate of decomposition is so generally regarded as a fundamental difference between mull and duff, as well as between better and poorer duff conditions, that it seems unnecessary to verify this by references. Statements in case can be found in almost any recent work touching upon the subject of humus forms. This is true whether or not the author in question still believes in a general poor aeration in the duff type. It is sufficient to refer to some of the most recent textbooks and summaries (8, p. 188; 17, p. 321–323; 43; 54; 65; 53, p. 524). P. E. Müller himself, in his later writings, apparently stressed the rate of decomposition more than he did in his early works (41, p. 208, 211; 42, p. 93).

Significance of the humus content

The curious thing is that the universal belief in the rapid decay in the mull and the comparatively slow decomposition in the duff is scarcely based on actual tests of any sort. It is true that both the direct observations in the field and the determinations of humus content seem to indicate so definitely a difference in the direction postulated that it may seem unnecessary to make an effort to prove it. The good crumb mull is usually covered with a loose layer of litter hardly more than 1 year old. It has a low humus content, often (especially in Europe) as low as 10 per cent or lower. The duff includes still recognizable remains from many years of litter-fall, and has a humus content often amounting to 80 or 90 per cent or even more. Thus a duff layer of 1 dm. thickness might seem to represent an enormous accumulation of humus as compared to a mull layer of the same thickness, and the common belief is that it does. It seems somehow to have been forgotten that the low figures for the humus content of the crumb mull are due largely to the fact that they are currently expressed on a weight basis. For a systematic comparison of the humus accumulation, the figures should, of course, be expressed on the basis of volume, or on a unit area of soil down to a certain depth.

Two things have probably tended to distract the attention from the humus content of the crumb mull, and to focus it somewhat one-sidedly on the unincorporated humus. One is the fact that outside of Scandinavia P. E. Müller's fundamental conception of the humus layer has never been commonly adopted. Thus the crumb mull is usually regarded as a part of the mineral soil, and is often left out of consideration in the discussion of humus accumulations. Another probable cause is a logical error which seems to have originated with Ramann (47, p. 141; 48, p. 154). He criticized the idea of Kostytschew that the amount of humus present was in inverse measure to the rapidity of decomposition, inasmuch as the humus must tend to accumulate until a balance is reached between the annual supply of organic matter and its decomposition. Ramann could not see how any regime of that sort could be established, and gave his own opinion in the words: "Accumulation will only take place where the formation of organic materials is more rapid than their destruction. The more this is the case, the greater the increase in quantity of the humus material will be; if both values are only slightly different, there will *seemingly* be a balance, such as has often been assumed." In other words, Ramann looks upon any humus accumulation as initiating a continuous piling up of organic

matter which will never stop as long as conditions remain unchanged. This idea, of course, is very apt to center the attention on the organic material on the surface, much of which is only imperfectly decomposed. This may partially account for the tendency to take for granted that any duff formation, or even the presence of any unincorporated humus, represents an abnormal, progressive accumulation, in contrast to a crumb mull condition, where the balance between litter production and decomposition is supposed to be perfect, or nearly so.

It is easily seen that Ramann's theoretical standpoint is wrong in principle. It would be correct if the forest soil could be compared to a cow and the annual litter-fall to the annual supply of hay reserved for this particular animal. The feeding capacity of the cow is limited, and if the hay supply is greater, some must be left for the next year, and so on. There would be a surplus of hay piling up from year to year. But the decomposition of the litter in nature is not taken care of by any particular animal with a limited food capacity, nor even by a fixed number of organisms. An increased supply means an almost immediate increase in the soil population taking part in the decomposition. With a heavier litter-fall, the total amount decomposed will be greater, and it seems reasonable to assume that, as long as secondary disturbing effects are not involved, it will increase in about the same proportion. In other words, it seems reasonable to consider the characteristics of any given combination of climatic and site factors, as far as decomposition is concerned, as the power of breaking down in a given time a certain *percentage* of the supply of fresh litter, whatever its absolute amount.

The decomposition of any particular batch of litter will proceed at a decreasing rate, as time goes on, following a curve characteristic of the particular litter and of the type of decomposition involved. If the litter-fall is doubled, there will be twice as much to decompose, and twice as much actually decomposed, the first year. There will also be twice as much left for the same or other organisms to work on, the next year, and they in turn will do twice the work, until complete decomposition occurs. If a level of doubled annual litter-fall is maintained, material of different age-classes will pile up until the combined annual loss (which is mainly due to decomposition) corresponds to the annual gain in the form of litter. When this regime is established, the actual amount of material present will be exactly doubled, compared to the earlier conditions with half the amount of annual litter-fall.[3] On the other hand, if the rate of decomposition could be altered without changing the characteristic curve representing the course of the decomposition, such a change would have the same effect as increasing or decreasing the amount of annual litter-fall. Halving the rate of decomposition would mean simply that everything which took one year before will take two years now. When the new regime is established, there will be twice as much material present as before, if the litter-fall has remained the same.

Kostytschew's idea is consequently right in principle. With a given litter-fall, the amount of organic matter present on and in the soil under balanced conditions ought to be a certain measure of the rate of decomposition characteristic of the particular environment. It must be stressed, however, that it cannot be a very accurate measure, not even under strictly virgin conditions. It is hardly imaginable that two different environments will be characterized by widely different *rates* of decomposition without the *type* of decomposition also being different and consequently the characteristic decomposition curve.

[3] This reasoning requires, of course, that the earlier conditions had lasted long enough, so there was another regime established before the doubling of the litter-fall. It is also required that all other conditions, except the amount of litter-fall, have remained unchanged. The latter condition, it is true, will hardly ever apply *exactly* to an actual case; no doubt an incipient humus accumulation, to whatever cause it is due, will as a rule imply or entail a certain change in the conditions governing the decomposition.

Closer comparisons will be permissible only between humus layers of approximately the same type.

Although this reservation has to be made, it is of interest to compare the amount of organic matter accumulation, even with different *types* of humus layer. If the current view is correct, that the essential differences are in *rate*, not in *type* of decomposition, such comparisons are perfectly legitimate. Therefore, if a comparison should fail to show a significant difference in humus accumulation between mull and duff, under comparable conditions, this would be enough to dispose of the ideas favored today.

Amount of humus in mull and duff profiles

Thus far, no systematic comparison of the main types of humus layer seems to have been made with respect to the humus content by volume or area. Only very few of the numerous humus determinations made have been recorded on such bases. Not even all of these figures can be directly used in a critical comparison, because data are lacking on thickness or type of the humus layer, or on the depth to which the determination was extended.

Some very instructive data have been collected by Vater and his collaborators (64). The thickness of the humus layer was measured in place (numerous measurements on each sampling spot were averaged), and on carefully cut-out samples of ¼ sq. m. size the dry weight and loss on ignition were determined. The data permit a computation of the amount of organic matter to the liter of the humus layer in place. Living roots were removed and thus are not included in the weight. All determinations refer to pine and spruce duff. The following figures, computed from Vater's data (64, p. 152, 170–173), show the organic matter content in kilograms to the liter.

SPRUCE DUFF		PINE DUFF	
Upper ("Moder")	Lower ("Torf")	Upper ("Moder")	Lower ("Torf")
0.06	0.07	....	0.08
....	0.14	....	0.15
0.09	0.24	....	0.09
0.12	0.15	0.10	0.16

The figures do not in general include the litter, which of course as a rule is still lighter (two determinations for the "Streu" layer on pine duff gave 0.04 and 0.10 kgm. to the liter). Only the first figure of upper spruce duff (0.06) includes some litter, which could not be removed from the F-layer. It is seen that Vater's figures for duff mostly lie near 0.1 and that only one exceeds 0.2 kgm. to the liter even for the lower and more compacted layer.

In crumb mulls, humus contents of 7 to 10 per cent by weight are not rare, even in Europe. In northeastern United States values above 10 per cent seem to be more common than those below 10 (52, table II, p. 589). The dry volume weight of a crumb mull usually does not differ very much from unity [the usual range is .8–1.0 (6, 55)]. Thus, the per-cent-by-weight figures can, for a rough comparison, be directly translated into kilograms to the liter by dividing by 100. The figures obtained are of the same order as Vater's, 0.1 kgm. to the liter. This means that *the ill-fated German "Trockentorf" does not necessarily contain more organic matter to the liter than a good crumb mull.* A 10-cm. layer of "Trockentorf," which is commonly considered as representing a very strong humus accumulation, may very well be matched in this respect by a good crumb mull.

Krauss and Grosskopf (22) determined the amount of organic matter on the surface of the soil in a number of German forests with "Auflagehumus" evidently including pronounced duff types. Their figures are expressed in weight per unit area and include the litter, the unincorporated humus, and also the washed-in soil humus, when this was considered necessary to get a true picture of the surface accumulation. The values in general lie between 5 and 15 kgm. to the square meter, although on moist sites in northwest Germany (Erdmannshausen; formerly Neubruchhausen) there are values as high as 40 kgm. to the square meter (estimated from the graphical tables, assuming that those lacking a reference scale are drawn to the same scale as the rest; this is the only way of using the data as they are presented). Except for these extreme values, the figures fail to indicate any stronger humus accumulation than can be found in good crumb mulls.

Auten (2) has some determinations of the weight of duff samples 1 foot square from different forest types on the Mont Alto State Forest in Pennsylvania. Rejecting his figure 1030, table 4, p. 28, which does not check with the data given on weight and thickness, and averaging the remaining 10 determinations, one obtains a weight of 652 gm. for a volume of 144 cubic inches. This is a volume weight of 0.276. Unfortunately, Auten does not give the loss on ignition figures for these particular samples, and there is a great variation in this respect in his material. Using his average figure, 55.5 per cent (2, p. 47), one obtains a humus content of 0.15 kgm. to the liter. This value, uncertain as it is, gives an interesting comparison with Vater's determinations.

A few additional data on volume weight and humus content of American duff forms were obtained in the writer's laboratory on samples taken by Mr. C. Heimburger in the Adirondack Mountains. The samples were taken using steel cylinders of Burger's (6) model (10 cm. high and of 1 liter capacity). Localities with particularly thick duff were chosen. One was a moss-rich red spruce flat, with fibrous duff, between Polliwog Pond and Middle Pond. The other was a hemlock ridge with a heavy greasy duff near Floodwood railroad station. Both were in the Saranac region. Only the H-layers were sampled. The figures obtained are as follows:

	FIBROUS DUFF	GREASY DUFF	
		Upper H	Lower H
Dry volume weight	0.14;0.145	0.18	0.245
Ignition loss, *kgm. to the liter*	0.12;0.12	0.12	0.14

These figures evidently corroborate the conclusions drawn in the foregoing from Vater's data, inasmuch as the values check very well with his. Even for the very compact-looking greasy duff the humus contents do not much exceed 0.1 kgm. to the liter. It should be noted that in these determinations *living roots were not picked out*, contrary to the procedure of Vater and of Krauss and Grosskopf. The values for the root-free humus would consequently have been still lower, no doubt especially so for the fibrous duff. Vater in one case (64, p. 170) gives the weight of the roots picked out. They represented 16 per cent of the total fresh weight of the humus layer.

The figures hitherto presented pertain exclusively to the humus layer. It is evident, however, that in order to judge the amount of humus accumulation the organic content of underlying strata should also be taken into consideration. When the available figures are examined, it is at once clear that here great variations are to be expected. The following general considerations seem, however, to be warranted.

A crumb mull is in many regions typically combined with a "brown soil" profile (48, p. 533; 61). The humus content of the brown horizon often amounts to 3 per cent or more in

the upper parts of the layer (60, p. 129, 149; 23, p. 18). It decreases very gradually with increasing depth. A characteristic of a typically developed brown forest soil is that the colloid-rich horizon is very deep [often up to 70 cm. (61, p. 5)].

A pronounced duff, on the other hand, is typically associated with a podzol profile. The various types of podzol profiles are widely different. In some of them, the humus content of the accumulation horizon may rise to values not encountered in any brown forest soil. In others, the humus content may be low throughout, even in the horizon of accumulation. The leached layer, too, sometimes contains very considerable amounts of humus, whereas in other cases the quantity is small. If the particularly humus-rich types of podzol profiles, associated with a more or less swampy condition, are excluded, there remains among the rest a widely distributed type of forest podzol profile: the iron podzol of Frosterus. This is typical of large stretches of coniferous forest with fibrous duff on normally drained soil (59, p. 55; 62). Frosterus (16) states as one of its characteristics that the humus content of the illuvial horizon is below 3 per cent (in another place: usually below 3). Now in this type the illuvial horizon is normally richer in humus than any other horizon of the mineral profile. Furthermore, the horizon usually fades out rapidly with increased depth (59, p. 58), so the well-developed part of it certainly averages less than the brown layer of typical brown forest soils. All this does not indicate in general any greater accumulation of humus in the mineral soil under fibrous duff than in the brown forest soil under mull.

More significant than such general considerations are direct numerical comparisons of duff and mull profiles, preferably in the same region. Unfortunately, very few figures are available of total humus content, expressed on the basis of volume or area. Consequently resort must be made to the usual per-cent-by-weight data, reasonable volume weight values being assigned to the different layers of the profile. In the computations, the following volume weights have been used throughout: 0.8 for crumb mull, 1.0 for the upper and 1.2 for the lower brown soil; and 1.5 for all mineral horizons of podzol profiles, as well as for the subsoil in all profiles. The figures are chosen with a view of being certain that the humus content of the brown forest soil profile with mull is not calculated unduly high as compared to the podzols with duff. For the same reason, the depth of 1 m., to which the computation has been extended, has been counted from the top of the mull in mull profiles, but from the top of the mineral soil in duff profiles.

A comparison has been made on this basis between three type profiles from Sweden chosen and carefully described by Tamm. The first is a very typical brown forest soil profile with mull from Hissön, province of Småland, south Sweden (23, p. 16–18; 57, p. 168). The humus content to the square meter was estimated as follows:

11 cm. crumb mull = 110 l. = 88 kgm. with 9.7 per cent humus, makes	8.5 kgm.
17 cm. upper brown soil = 170 l. or kgm. with 4 per cent humus, makes	6.8 kgm.
28 cm. lower brown soil = 280 l. = 340 kgm. with about 2 per cent humus, makes	6.8 kgm.
44 cm. subsoil = 440 l. = 660 kgm. with about 1 per cent humus, makes	6.6 kgm.
Total humus content to the square meter down to 1 m. depth	28.7 kgm.

To this figure should be added the organic matter of a litter cover 2–3 cm. in depth.

For comparison, two duff profiles from northern Sweden have been chosen, representing different shades of the iron podzol as developed under the influence of spruce forest of the *Myrtillus* type, the strongest duff-forming and strongest podzolizing among all the forest types of north Sweden occurring on normal, not swampy, ground (59, pp. 154, 159, 166). The first locality, representing, it seems, the purest "*Vaccinium*" type of Malmström (34, 35), is near Håsjö, province of Jämtland, near the geographical center of Sweden (59, pp. 249–

250; 62, pp. 325–327; 23, p. 34). Assuming for the humus content of the (fibrous) duff the rather liberal figure 0.15 kgm. to the liter (cf. the foregoing), the estimate runs:

4 cm. duff = 40 l., estimated humus content 0.15 kgm. to the liter, makes	6.0 kgm.
8 cm. leached layer = 80 l. = 120 kgm. with 2.2 per cent humus, makes	2.6 kgm.
10 cm. rust-brown layer = 100 l. = 150 kgm. with 3 per cent humus, makes	4.5 kgm.
82 cm. subsoil = 820 l. = 1,230 kgm. with 1.2 per cent humus, makes	14.8 kgm.
Total humus content to the square meter down to 1 m. depth,	27.9 kgm.

To the figure should be added the organic matter of a litter cover 1–2 cm. thick.

The second duff locality seems to represent a somewhat moister variant of Malmström's "*Vaccinium*" type (with *Dryopteris Linnaeana* and *Cornus suecica*) from Rokliden, province of Norrbotten, north Sweden (59, pp. 246–247; 62, p. 327; 23, p. 35–36; 57, p. 168). The analyzed profile was exceptional in having a very heavy, hard ortstein, the upper 15 cm. of which were dark brown. The estimate works out:

7.5 cm. duff = 75 l., estimated humus content .15 kgm. to the liter, makes	11.3 kgm.
20 cm. leached layer = 200 l. = 300 kgm. with 1.4 per cent humus, makes	4.2 kgm.
15 cm. upper ortstein = 150 l. = 225 kgm. with 2.5 per cent humus, makes	5.6 kgm.
30 cm. lower ortstein = 300 l. = 450 kgm. with 1.7 per cent humus, makes	7.6 kgm.
35 cm. subsoil = 350 l. = 525 kgm. with .6 per cent humus, makes	3.2 kgm.
Total humus content per square meter down to 1 m. depth,	31.9 kgm.

To the figure should be added the organic matter of a litter cover 2–3 cm. thick.

Considering the approximate nature of the estimates, the three values obtained might well be regarded as identical. In the first locality, the mull was, in places, 15 cm. thick, which would make the figure of the total humus content 31 kgm. to the square meter instead of 29. Conversely, if in the estimate for the last locality the more conservative and probably better value .12 is used instead of .15 for the humus content of a liter of duff, the total humus content would become 30 kgm. to the square meter instead of 32. The result of the comparison should then be expressed thus: *A type profile of brown forest soil with crumb mull from south Swedish beech-woods shows as high a total humus content as either of two type profiles with pronounced duff from the strongest duff-forming and podzolizing forest type on normally drained ground in northern Sweden.*

Hardly anyone would have expected this result from an ocular comparison of the two profiles from Hissön and Rokliden.[4] It also controverts absolutely ideas current in the literature. The writer recalls only one statement of recent date which allows any possibility of such a result. This statement is found in P. E. Müller's latest work (42, p. 96). In discussing the amount of nitrogen contained in heath soil he says that this depends on the amount of humus, "which in heath areas with a thick duff cover *in general* exceeds that of the mull *on the same sandy soil.*" (The italics are mine.) In order fully to realize the remarkable cautiousness of this statement it must be remembered that the typical profile of the Danish heaths with its heavy, compact duff, its strongly humus-impregnated, partly black and greasy leached layer, and its partly black ortstein (66, plate I) gives every indication of representing a particularly strong humus accumulation. It should also be remembered that the mull in the oak scrubs representing the mull islands in the heath is particularly light in color and poor in humus. Nevertheless, P. E. Müller by his "*in general*" grants the possibility of the heather profile being not *always* the richer in humus, not even when it has "a thick duff cover." Furthermore,

[4] Both these places have been visited by the writer.

only the mull *"on the same sandy soil"* is included in the comparison, not mull or crumb mull in general.[5]

The chief reason for the apparently common error of judgment concerning these matters is probably a theoretical conviction that the pronounced duff profiles *must* represent a particularly strong accumulation of humus. Secondly, there is an overrating of the humus content of humus layers of the duff type, because so very few determinations of their volume weight have been made.

The comparisons just made of course do not necessarily show anything about the rate of decomposition in the different types, because there is no guarantee that the annual litter-fall is comparable in the different localities. No determinations seem to have been made of the litter-fall of north Swedish softwoods but there is reason to believe that at least in the northernmost locality it is considerably smaller than in the beech forest in south Sweden where the first profile was located (cf. foot-notes 6 and 11).

Data which would seem to permit a comparison under conditions of about equal litter-fall are reported in a paper by Bujakowsky. He gives (5, p. 263) figures of "total organic matter" in kilogram to the square meter for a number of localities in German spruce forests (of different history, it is true; some following oak, some pine, some spruce, etc.). The data, however, do not represent the total organic matter down to a standard depth. Only the strongly humus-impregnated surface layer has been taken into account, down to a depth varying from 5 to 40 cm. (in most cases 5–10 cm.), counted from the top of the "mineral soil" (personal communication from Dr. Bujakowsky). For instance, in the most pronounced crumb mull profile (No. 1) only a 5- or 6-cm. surface layer has been considered, out of "20 cm. loam rich in mull, well crumbled." It seems evident that Bujakowsky's "totals" are grossly misleading, particularly for the mull profiles; they can hardly be used for a critical comparison.

Some very significant figures have been recorded recently by Morgan and Lunt (37). They compared the total amounts of organic matter down to a depth of 40 inches in two pairs of profiles of different type, situated two and two in the same neighborhood (one pair in the White Mountains and one in Connecticut). Translated into kilograms per square meter and given in condensed form, their figures are:

Data given on locality	*Total organic matter* kgm. per sq. m.
Thick podzol, Waterville, N. H.	62.1
Rich crumb mull, Bethlehem, N. H.	57.8
Thin podzol, Union, Conn.	30.4
Crumb mull, Groton, Conn.	24.9

Of the four profiles studied by Morgan and Lunt, two represent localities visited by the writer: the Waterville tract and the crumb mull locality at Bethlehem. What makes Morgan and Lunt's figures particularly significant and interesting is that the Waterville tract is believed to represent a virgin forest (red spruce, with some admixture of hardwoods) except for the parts where cuttings have been started recently, after the tract was made a part of the White Mountain National forest. In the places examined by the writer, the humus layer was a typical greasy duff, sometimes very heavy (52, Table X, samples 119–121), in fact, much

[5] In fact, the humus accumulation in the Danish heaths does not seem to be excessive. From data recently reported by Weis (66, p. 31, 45, 49) from a virgin heath with a "rather thick" heather duff and a "very strong" hardpan (including a thick, black humus pan), the total organic matter accumulation down to 1 m. depth can be estimated at about 40 kgm. to the square meter. This figure should be compared with some data reported in the following for mull profiles.

heavier than it could have been in the profile studied by Morgan and Lunt. Which one of the two profiles is more representative of the tract, the writer is unable to tell. At any rate it is very remarkable that Morgan and Lunt's Waterville profile— whether chosen at random or with a view of representing average conditions—has yielded so nearly the same total amount of organic matter per unit area as the crumb mull profile at Bethlehem. The latter locality has been described in detail elsewhere (52, appendix p. 16–18). The crumb mull is perfectly typical morphologically. Only it is unusually deep and rich in humus, judged from European experience. The near identity of the total amount of humus in Morgan and Lunt's two profiles from the White Mountains would certainly be surprising to anybody who has seen the profiles.

The general result of the comparisons made is that a typical crumb mull profile may represent just as high an accumulation of organic matter as does a very pronounced duff profile, even when conditions are fairly comparable. *There is no indication of a consistent difference between the crumb mull and even pronounced forms of duff in the amount of organic matter stored up either in the humus layer or in the entire profile.*

Of course the writer does not intend to deny the possibility of a certain average difference between mull and duff in amount of accumulated organic matter. It is realized that there are duff profiles which represent an accumulation of organic matter hardly matched by any crumb mull profile. As an example, the following profile with 40 cm. greasy duff may be quoted (Hemlock ridge near Floodwood station, Saranac region, Adirondacks, sampled by C. Heimburger).

	kgm. per sq. m.
4 cm. litter and F layer, estimated at	4.0
21 cm. upper H layer, 210 x 0.1225	25.7
16 cm. lower H layer, 150 x 0.144	23.0
4 cm. leached layer, 40 x 0.017	0.7
20 cm. ortstein, 200 x 0.105	21.0
20 cm. transition zone 200 x 0.023	4.6
56 cm. subsoil 560 x 0.0085	4.8
Total organic matter content down to 1 m. depth	83.8

Even a humus accumulation of this impressive amount does not necessarily mean, however, that the decomposition is excessively slow. It is true that 84 kgm. to the square meter probably equals 200 years or more of the annual leaf-fall;[6] but to the latter has been added, in the virgin forest, about an equal amount (9, p. 68) of organic matter from logs. The accumulation, therefore, probably corresponds to no more than between 100 and 200 years' total litter

[6] The determinations made in central Europe on different species have mostly given values ranging between 0.3 and 0.5 kgm. organic matter to the square meter, with a surprisingly small variation according to site and species (9, 63), exceptionally as low as 0.2 (7) or as high as 0.6. In Danish beech woods, C. M. Møller found values all ranging between 0.2 and 0.3 (unpublished data read August 1929 at the 18th meeting in Copenhagen of northern naturalists; kindly communicated by Prof. Møller). In Jack and Norway pine stands in northern Minnesota, Alway and Zon (1) found as low an average as 0.2. Auten (2) finds in Pennsylvania 0.3 for the ridge, 0.4 for the slope, and 0.6 for the cove type. Unpublished data kindly furnished by Professor Geo. S. Perry, of Mont Alto, Pa., give the values 0.3 for pitch pine, 0.5 for red pine, and 0.6 for white pine stands in Pennsylvania.

production. On the other hand, it represents probably the total result of accumulation from thousands of years of forest growth, maybe all since the glacial period. The greasy duff will not easily burn at any season of the year.

Still it should not even be contested that in particular cases there may actually be a "practical standstill of decomposition," as duff formation has frequently been interpreted in Germany. Some data reported from northwest Germany seem in fact to indicate a really amazing accumulation during a single rotation (see for instance 21, p. 429).

Soil respiration

The production of carbon dioxide gives a fairly good idea of the total decomposition going on in materials like snuff, composts, manure, or soil. It would seem, therefore, that a determination of the CO_2-evolution, or so-called respiration, of the soil in place would furnish an excellent means of comparing the rapidity of decomposition in different types of humus layer or soil. In fact, the various authors engaged in such determinations during the last decade frequently have used their results for interpretations along that line. Lundegårdh expresses the idea very clearly: "As would have been expected, the true mull soils respire most intensively, raw humus soils more weakly" (28, p. 182). Later, he was much surprised to find that duff soils also may have a considerable respiration (33, p. 381). Fehér tries to bring the respiration values in parallel to the results of bacterial counts, although not always with success (14, p. 482). It is easily seen, however, that this reasoning cannot be correct, as far as stable natural conditions are concerned. With slow decomposition, more material will pile up than with more rapid, but when a regime is established, the respiration will be exactly equal in both cases, under otherwise equal conditions, particularly if the litter-fall is the same and if there is no difference in the root respiration. *Determining soil respiration under balanced natural conditions is measuring the annual litter-fall plus the root respiration, but not the rapidity of decomposition.*[7]

Yet the data cannot be ignored. It must be realized that the authoritative statement by Lundegårdh, quoted in the foregoing, is incompatible with the conclusion just presented. It is well known that with the same species and apparently very much the same litter-fall either a good crumb mull or a bad duff might form. The beech, for instance, is at the same time one of the best "soil-improvers" and one of the worst duff-formers. According to Lundegårdh's statement, which is based on data from beech forests, beech mull would show a consistently stronger respiration than beech duff. From the reasoning given in the preceding paragraph, this would not be expected, under balanced conditions.

Table 1 gives a synopsis, aiming at completeness, of the available material from European forest soils in place. (Some determinations from this country are reported in the following section.) The table also includes forest soils worked according to silvicultural practices, and soil of cleared areas. Some of these data will be of use for later reference. Treeless heath-

[7] It is true that in dealing with artificial conditions, it might be quite different. There the method will in many cases be of value in studying the immediate effect of silvicultural measures on decomposition. Effects of that kind will be discussed in a following part of the paper. Here we are primarily concerned with the differences between natural types of humus layer. It is evident from what has been said that we cannot expect to get much pertinent information on that point from data on soil respiration alone.

TABLE 1

European determinations on respiration of forest soils

REFERENCE	PERIOD	LATITUDE, °N.	STAND	GROUND VEGETATION	HUMUS LAYER	RESPIRATION, GM. CO_2 PER SQ. M. PER HOUR			N	METHOD
						Maximum*	Minimum*	Mean		
51, p. 32	VIII.24–IX.4	63	Pine (2 stands)	Moss-rich type	Duff	0.62	0?	0.22; 0.49	10; 12	acc
45, p. 124	V.31–VI.1	60⅓	Spruce + pine	Oxalis-Myrtillus type	Duff	0.60	0.19	0.47	13	vent
45, p. 125	VII.3–4	60⅓	Spruce + pine	Oxalis-Myrtillus type	Duff	1.28	0.56	0.84	25	vent
45, p. 126	VIII.24–25	60⅓	Spruce + pine	Oxalis-Myrtillus type	Duff	1.01	0.60	0.85	25	vent
51, p. 32	VII.28–VIII.30	59	Pine (2 stands)	Moss-rich type	Duff	1.11	0.32	0.54; 0.54	38; 51	acc
10, p.328†	VIII.28–IX.11	56½	Pine	Grass, moss, Myrtillus, etc.	Duff	0.45	0.22	0.30	45?	acc
24, p. 68	VIII.31	56½	Beech	None	Mull‡	0.38	0.35	....	2	sim
50, p. 145	VI.29–VII.2	56½	Beech	Scarce; mixed type	Duff	0.25	0.14	0.18	4	acc
10, p. 326†	VII.14–VIII.3	56½	Beech	Scarce; mixed type	D 6–12 cm.	1.2	0.5	0.87	63?	acc
25, p. 352	X.10	56½	Mixed hardwood	Rubus idæus, Oxalis	Mull‡	0.08		....	1	acc
24, p. 68	VIII.11–21	56½	Alder	Oxalis	?	0.25	0.20	0.23	3	sim
24, p. 68	VIII.12; VIII.21	56½	Alder	Circæa; Swamp vegetation	Muck?	0.21	0.17	....	1; 1	sim
25, p. 352	X.10	56½	Alder	Oxalis, Aspidium; Viola palustris	Mull‡	0.12	0.07	—; 0.07	1; 2	acc
25, p. 352	X.10	56½	Alder	Oenanthe aquatica	Muck	0.03		....	1	acc
25, p. 352	X.10	56½	Alder	Majanthemum bifolium	Duff‡	0.03		....	1	acc
26, p. 137	?	56½	Alder	Not given ("swamp")	Muck?	0.12	0.03	....	2	?
27, p. 24	VIII.22‖	56½	Alder	Oxalis‖	Mull‡	2.34		....	1	acc
10, p. 324†	VII.1–6	56½	Alder	Mixed, mostly swampy	Muck	0.36	0.15	0.24	18	acc
36, p. 39	VIII.10–30	53¼	Spruce + pine	None	5 cm. Li + F	0.83	0.43	0.57	19	sim
36, p. 40	IV.17–V.7	53¼	Spruce + pine; spruce	None, or Polytrichum	4–8 cm. Li + F	0.45	0.15	0.27; 0.18	21; 6	sim

36, p. 39	VIII.12–24	53¼	Spruce + pine	— (soil recently worked)	.....	0.70	0.48	0.60	5	sim
36, p. 40	IV.18–24	53¼	Spruce + pine	— (same next spring)	.....	0.18	0.13	0.15	3	sim
36, p. 39	VIII.10–31	53¼	Pine stands	Mosses, or no vegetation	Partly D	0.58	0.30	0.39; 0.57	10; 3	sim
36, p. 40	IV.17–V.1	53¼	Pine	Mosses, or no vegetation	Partly D	0.26	0.14	0.19	15	sim
36, p. 72	VIII.22–IX.9	53	Pine stands	Mostly grass (some worked)	Sod	0.93	0.25	0.48	29	sim
36, p. 72	IX.3–9	53	Clear cuts	Mostly grass, mostly worked	.....	0.73	0.21	0.44	10	sim
36, p. 72	IX.5; IX.8	53	Clear cut	*Just thoroughly worked*	.....	1.35	1.17	....	2	sim
36, p. 50	VII.4–24	52¾	Pine + hardwood	Duff plants	Duff	0.99	0.39	0.62	46	sim
36, p. 50	VII.8; VII.11	52¾	Pine + hardwood	*Duff recently turned over*	Duff	1.40	1.13	....	2	sim
36, p. 50	VII.6–24	52¾	1 Beech; 2 Oak	Polytrichum, or no vegetation	Mostly D	0.70	0.53	0.60	6	sim
36, p. 63	VIII.4–18	52	Pine	Moss, Cladina, or none	Mostly thin	0.65	0.30	0.45	34	sim
36, p. 113	VII.19	52	Pine	Moss, Cladina, or none	Mostly thin	0.50	0.18	0.33	9	acc
36, p. 63	VIII.5; VIII.7	52	Beech under pine	Some Polytrichum	8 cm. FD	0.59	0.57	....	2	sim
36, p. 161–170	VI.2–XI.24	51½	Spruce	None, or mosses, etc.; some Rubus	4–10 cm. D	0.54	0.07	0.31	25	acc
36, p. 163–166	VI.2–XI.10	51½	Beech; oak + beech	Few grasses, moss, Myrtillus	Up to 10 cm. D	0.84	0.10	0.36	21	acc
36, p. 166–169	VI.6–XI.15	51½	Beech; oak + beech	None, or Oxalis and some moss	Mull	0.72	0.13	0.33	35	acc
36, p. 170	X.2; X.17	51½	Pine	Myrtillus, Leucobryum	7 cm. D	0.30	0.20	....	2	acc

* The values given as maxima or minima as a rule represent single determinations, but in Fehér's series from Hallands Väderö (= 56½° lat. N.) they are averages for a day (representing each three determinations) and in the same author's 12-month series from Sopron (= 47½° lat. N.) they are averages for a month.

† Fehér's values from Hallands Väderö as originally given were 10 times too high, because he had used, without checking, the erroneous formula published by Lundegårdh (27, p. 7; 28, p. 146; 30, p. 420) and reprinted by Stoklasa and Doerell (56, p. 688), for computing the results using the accumulation method. The error was pointed out by Romell (51, p. 56), and in later papers by Fehér the data from Hallands Väderö are quoted with their correct values (except 13, table 4, p. 28, where by mistake the original values still stand). The values given here are the corrected ones.

‡ These are Lundegårdh's indications as to the type of humus layer (28, p. 182).

‖ Date and ground vegetation as given by Lundegårdh (30, p. 420, and 28, p. 181).

TABLE 1—*Concluded*

REFERENCE	PERIOD	LATITUDE, °N.	STAND	GROUND VEGETATION	HUMUS LAYER	RESPIRATION, GM. CO_2 PER SQ. M. PER HOUR			N	METHOD
						Maximum*	Minimum*	Mean		
36, p. 35	VII.6–26	50½	Spruce	None	Weak duff	0.63	0.36	0.47	12	sim
36, p. 35	VII.12–25	50½	Spruce + hardwood	Moss, grasses, some herbs	"Well decomposed"	0.72	0.55	0.63	9	sim
15, p. 255	VII.15–25	47¾	Oak	Rich herbaceous vegetations, ferns and moss	Mull	1.4	0.8	1.06	11?	acc
15, p. 257	VII.26–VIII.8	47¾	Pine + hardwood	Few herbs, Pteris, Polytrichum	Mull?	1.15	0.7	0.88	14?	acc
15, p. 258–259	IX.1–13	47½	Spruce + hardwood	Hazel, herbs, some Myrtillus	Mull?	0.85	0.2	0.56; 0.56	13; 3?	acc
15, p. 260	IX.13–16	47½	Spruce + larch	Mull mosses	Mull	0.7	0.5	0.58	4?	acc
12, p. 423	12 months	47½	Spruce	Rich herbaceous vegetation, mull mosses	Mull	1.26	0.07	0.58	360?	acc
14, p. 474	VII.30–VIII.14	47	Robinia	Grasses, few herbs	?	1.83	0.03	1.21; 0.56	13; 12	acc
14, p. 477	VIII.31–IX.7	46¼	Robinia	Anthriscus trichospermus, Equisetum ramosissimum	?	1.60	0.72	1.18	7	acc
14, p. 477	VIII.31–IX.7	46¼	Austrian pine	None	Duff	1.39	0.04	0.85	7	acc

The figures in the "Reference" column refer to the bibliography. The Roman numerals under "Period" refer to the months, and the Arabic numerals, to the days of the months indicated. The latitudes north are approximate. The humus layer has been labeled either from direct statements on its type made by the respective authors, or by inference from other data given (description, vegetation). A question mark indicates that the labeling is reasonably safe in spite of somewhat insufficient or contradictory indications. The abbreviations in the "Humus layer" column mean: D = duff, F = F-layer, FD = fibrous duff, Li = litter, M = mull (52). The column "N" gives the number of determinations represented by the preceding data. For the last column, see "Comments on methods." Part of Fehérs values have been taken out from his graphs, and the second decimal might in these cases be wrong. The same applies to all of Porkka's values. In some cases, as is seen, the second decimal is not even given.

land and meadows have been left out. Three values reported by Stoklasa and Doerell have been omitted because of the absence of data on analytical methods used and data as to location.[8]

Before quoting the figures, a few comments on methods will be given. They will be of use in judging some of the data, and also for later reference.

Comments on methods.—There are three types of methods, which will be referred to as the "simultaneous absorption," the "accumulation," and the "ventilation" methods (abbreviated in table 1 as "sim," "acc," and "vent" respectively). All three have in common the fact that a small area of soil is isolated under a bell or box, into which the CO_2 diffuses from below. In the *simultaneous absorption* method (4, 24) the CO_2 is absorbed, as it diffuses from the soil, by an alkaline solution contained in a flat vessel placed under the bell. With the *accumulation* method (50, pp. 143–144), the CO_2 gradually accumulates under the bell, where no absorbing agent is present. The rate of accumulation, which is determined on withdrawn air samples, measures the respiration intensity. In the *ventilation* method [proposed independently, it seems, by three different parties (56, p. 689; 20; 44)], the CO_2 evolved from the soil is carried away by a current of air and conducted to an absorption apparatus.

Meinecke (36, p. 106) compared the simultaneous absorption and the accumulation methods and found about 10 per cent higher results for the former. Romell (51, pp. 40–41) pointed out that this result cannot be generalized, and explained the relatively good check obtained by Meinecke as due to the rather long time (24 hours) that he ran his absorption tests. The simultaneous absorption method will in general give more reliable results with a *long* duration of the experiment (51, p. 41), provided the absorption is satisfactory.

With the accumulation method, the tests should be made as *short* as is possible for analytical reasons. The degree of approximation to the true values with this method depends in principle merely on the accuracy of the methods for measuring the CO_2 accumulation. Thus the most sensitive analytical methods should be used, and Fehér (11) did well in replacing the awkward apparatus recommended for the purpose by Lundegårdh (28, p. 147) by a more reliable one (Lundegårdh's bell apparatus). On the other hand, with Fehér's use of this combination, there is the possibility of unexpected errors which might be serious. Fehér takes out for analysis .6 to .8 liters, from a diffusion bell having a cross section of about .07 sq. m. This means that when taking his sample for analysis, he sucks out the air contained in the surface soil down to a depth which, with an air space of 40 per cent, amounts to 2–3 cm. Now the CO_2 content of the soil air, even in the surface soil, frequently counts in tenths of a per cent, not in hundredths, as in the free air. The error introduced in the analysis by this excess CO_2 will depend on conditions, for example, on how much of the soil air will actually

[8] Some reader may miss the data given by Lundegårdh in his several later publications. His original data are, however, all in the table. But most of them are difficult to recognize, from his later publications, because a most curious series of calamities happened to them when Lundegårdh compiled the table on p. 181 in his book of 1924. Numbers 7–13 in this table are evidently quoted from Lundegårdh (25, p. 352) but have become 10 times higher than before. [It is regrettable that Lundegårdh did not compute a "diffusion number" for No. 7, as he did for Nos. 8–9, 11–12, because that would have given him a value higher than what he concludes (28, p. 160) to be the highest possible, and thus would have shown him that something was wrong with the figures.] Numbers 14–16 of the table are expressedly quoted from Lundegårdh (24, p. 68) but are still more difficult to recognize, having become about 4.2 times higher than they originally were. A condensed result of these slips has unfortunately been perpetuated not only by Lundegårdh himself (29, p. 361; 30, p. 420; 31, p. 408; 32, p. 269; 33, p. 381), but also by Dengler (8, p. 160), partly by Russell (53, p. 311), and possibly by others. In these condensed tables, there is the further slip that the two last lines of the table (28, p. 181) have been interchanged, so the figures which in 1924 referred to "fucoid beds on the shore" have come to stand for "beech forest."

reach the opening of the sampling tube and be drawn out into the analyzing apparatus. With perfect stirring during sampling, half of the soil air will be included with the sample. Assuming a CO_2 content in the soil air of .2 per cent, which is hardly an extreme figure, this would make the value determined about 30 per cent too high in a model case quoted by Féher (11, p. 354).[9]

The ventilation method presents a number of obvious technical difficulties, but seems to be without objection in principle, provided the ventilation is effected by atmospheric air and the arrangement is such that the outside pressure is maintained within the bell. (This seems to apply to Porkka's use of the method.)

In judging the figures contained in table 1, it should be noted first that none of the workers engaged in collecting the data has been concerned with the problem of comparing definite natural types of humus layer. The studies were made with other views in mind. This explains why such a great deal of the material refers to forests planted on old heath-land (Meinecke), plantations on sand plains (Fehér), and other artificial conditions with humus layers which are often difficult to classify, at least from the descriptions given. Only the Swedish-Finnish material (the localities between 63° and 56½° lat. N.) is chiefly composed of determinations from natural forests. Unfortunately, this material very one-sidedly represents the duff type. The only localities labelled as "mull" are all on the little island of Hallands Väderö, and even those are not representative. The good Swedish material from duff soils could for our purposes hardly be used otherwise than for a comparison with material from localities far away.

The sandy and gravelly soil of the granitic island Hallands Väderö in the climate of the western Swedish sea shore permits a typical mull to form only in places, and hardly under pure beech. In the alder swamps, the mull, if it forms at all, is of the detritus mull type, if the writer recalls correctly. Thus a good crumb mull locality has hardly been included in the studies made in Fennoscandia, except possibly Lundegårdh's single determination rather late in the fall in a "mixed hardwood" stand on Hallands Väderö. Moreover, even if Lundegårdh's "mull" localities are all accepted as such, they represent very few determinations. Because of the dominating rôle they have played in the literature, however, the data from Hallands Väderö will be discussed separately later.

In the German material, too, the localities clearly representing mull conditions are scarce. Only some of the beech stands in Gahrenberg (51½° lat. N.) can with certainty be labelled as good mull localities. Fortunately, the series obtained in these Gahrenberg localities are long and representative, and parallel series were run simultaneously in beech stands with pronounced duff. Thus in this case a significant comparison is possible. *It is seen that neither the extremes nor the averages indicate any significant difference.* In fact, the figures for the stands with mull appear a little *lower*. At least two of the three mull localities included in these series seem from the description to have a clear crumb mull and brown forest soil profile.

The Hungarian material, contrary to the more northern material, mostly represents mull soils, or at any rate soils without duff (some of the localities may hardly have a forest humus layer at all). In fact, only one duff locality is included (labeled as such by Fehér). This one locality is a plantation of Austrian pine at Szeged (46¼° lat. N.) and only seven determina-

[9] Possibly Fehér's values might be too high also for another reason. The time taken as the duration of the test is given as the time "between the closing and the opening of the bell." This is far from being clear, but if it means the time between putting in the stopper in the neck of the diffusion bell and sucking out the sample, there is a possibility of a certain unintentional and undetermined accumulation of CO_2 in the bell before the experiment was taken to start. (It seems that the CO_2 value at the start was determined not on a sample drawn from the bell, but in the open air.)

tions were made there. The results average considerably lower than seven parallel determinations in a near-by locust plantation. This could be taken as an argument in favor of Lundegårdh's contention, but it cannot be considered a very strong one. Not only are the determinations few, but the localities at Szeged represent highly artificial and hardly stabilized conditions (17–43-year old plantations on the puszta), so the values obtained cannot be considered as having much bearing on our problem. It should be noted, further, that even the duff locality yielded a high mean and a high maximum value. Both are higher than the corresponding averages for the rest of the Hungarian material.

There remains the possibility of getting something out of a general comparison between mull and duff averages from table 1, independently of the season and the geographical location. One could possibly hope that the extent of the material would be sufficient to offset the disturbing influence of variations of various kinds. Accepting for a moment this reasoning to be justified, one will be surprised, first, to see that the highest mean values north of Hungary have been encountered not in Germany, but in Finland and Sweden. It is noted that these high northern averages represent clear duff types.[10] For the rest, the mean values mostly lie, rather evenly distributed, between 0.2 and 0.7 gm. of CO_2 to the square meter per hour throughout Sweden, Finland, and Germany. The mean value of the long and representative series from mull soils at Gahrenberg in southern Germany is .33 gm. to the square meter and consequently does not rank particularly high, in spite of the fact that these localities mostly represent site-class II (in one case III) for beech.

The apparent lack of a general downward trend in the values towards the north, within the German and more northern material, is not as surprising as it might seem at first hand. It is true that the litter production is probably greater in some of the German material representing high site-classes than it is in the northern stands.[11] On the other hand, the length of the season favorable for decomposition must influence the values. With a longer growing season, the values per hour or day will average lower, under the same conditions of litter-fall, because the same amount of decomposition is distributed over a longer period. This is probably the explanation of the surprisingly high northern values.

All the more remarkable, then, do the high values from Hungary seem. Here the averages to about 50 per cent lie within the same range (of .2–.7 gm. of CO_2 to the square meter per hour) as in most of the more northern material, but the other 50 per cent are higher, some very much so. This is the case also with the one series from a duff locality. It is true that the

[10] Porkka does not tell anything about the humus layer in his localities, but it is apparent from the vegetation and the location (*Oxalis-Myrtillus*-type near Helsingfors) that it must be a clear duff type. Fehér fortunately gives data on the thickness of the duff in his beech forest on Hallands Väderö. When he calls a 6–12 cm. thick duff "relatively thin" (10, p. 326), it must be remembered that he believed at that time the hourly soil respiration to average 8.7 gm. of CO_2 to the square meter, high above Lundegårdh's earlier world's record of 2.34 gm. to the square meter (see the following), and that this, according to current views, must mean a particularly rapid decomposition and consequently the absence of any marked surface accumulation of humus. The beech forest where he worked represents only site-class V of Schwappach (51, p. 52).

[11] True enough, the litter-fall has been found to vary surprisingly little with the site-class (63). On the other hand, the percentage of the yearly production of dry matter which goes into litter-forming material has been found remarkably constant (9), and the production of wood, as is well known, varies markedly with the site-class. Evidently the absolute amount of litter-fall and the percentage of the production going into the litter cannot *both* be constant, independently of site-class. The explanation of the *relative* constancy of both values is probably that in the more productive stands the leaf-mass is *somewhat* increased, but not in proportion to the greater production, which is in part due to the assimilating apparatus working more efficiently under more favorable conditions of site.

highest values are from other localities, without duff. Thus the general high level of the Hungarian values could be taken as an argument in favor of a greater CO_2-production of mull than of duff soils. This argument cannot be given much weight because of the difficulty of a significant comparison.

There is, furthermore, the possibility that the Hungarian values are too high because of the method used (cf. "Comments on methods"). If the total evolution of carbon dioxide during a year is computed from the very interesting all-year series obtained in a spruce forest at Sopron (47½° lat. N.), one finds that it represents the amazing value of 1.39 kgm. of carbon to the square meter of soil, corresponding to the carbon content of over 3 kgm. of litter, which must be between 5 and 10 times the actual amount of needle-fall. Of course, the ground vegetation might have contributed a considerable share, and we do not know how much of the soil respiration is due to the roots. Still the result of the computation appears very high, too high to look quite reasonable.

The survey of the available determinations of carbon dioxide production by forest soils has given a somewhat disappointing result. In the whole material there is hardly more than one case where a significant comparison of mull and duff soils can be made. This one comparison shows no difference. Lundegårdh's contention that the true mull soils respire more intensely than the duff soils is, therefore, hardly supported by evidence.

Lundegårdh's attitude was in fact determined by data representing, in all, eight single determinations. Out of these, five were made on the same day in October when the hourly respiration was in most cases reduced from tenths to hundredths gram of CO_2 to the square meter. Of the three remaining determinations, which are said to represent "true mull" soils, two have given the perfectly normal value 0.4 gm. to the square meter which is greatly exceeded by many values for duff, even by averages of long series, obtained (by Fehér) on the same island. There remains the single value 2.34 gm. to the square meter, which is indeed very high, representing at present the world's record. This single value does not inspire confidence. It stands quite isolated among over 900 determinations from 63° down to 46° latitude, and is about 10 times higher than all the other data obtained from the same locality (alder forest on Hallands Väderö) during the same time of the year (July–August).[12]

In conclusion, the respiration determinations made on forest soils have shown a considerable variation, but most of the average values lie between 0.2 and 0.7 gm. of carbon dioxide to the square meter per hour. This holds true all the way from the northern part of Sweden at 63° latitude at least down to southern Germany. Thus the normal range seems to be rather different from what has been taught in textbooks for the last seven or eight years. The *minimum* figures exceeding 1 gm. to the square meter, given by Lundegårdh in a number of publications, seem to correspond approximately to normally occurring *maximum* values. Averages up to 1.3 gm. have been found in Hungary, by the use of a method which possibly gives too high values. Contrary to what has been taught, there is no indication of a consistently more intense respiration of mull soils, even crumb mulls, as compared to duff. The regrettable scarcity of the material available for significant comparisons is hardly the sole reason for this negative result. It is really to be expected, and this whether or not there is any difference in rate of decomposition be-

[12] Cf. footnote 2(†) to table 1. The excellent agreement obtained between the directly determined figure 2.34 and the CO_2 evolution from soil samples (27, p. 24) is hardly a proof that the value, or even its order of magnitude is correct [cf. van Suchtelen's remarkable findings on the behavior of isolated soil samples (58)].

tween mull and duff. The soil respiration cannot well be a measure of this rate, as it has been supposed to be. Under balanced natural conditions, it is rather a measure of the annual leaf-fall plus the intensity of root respiration.

A comparison between crumb mull and root duff under Northern hardwoods

In the preceding discussion, the lack of unquestionably comparable data on humus layers of different type is keenly felt. The determinations reported in the following are given as a modest contribution toward the filling of this gap. The work was planned with the view of finding an explanation of a certain discrepancy between field observation and some nitrification tests, reported in an earlier paper (52). With this in mind, it was decided to choose for a comparison the crumb mull and the root duff types of humus layer. The latter was chosen rather than some other form of duff, partly because of its surprisingly high nitrification during storage in the laboratory, partly because in the region root duff rather than more pronounced forms of duff can easily be found near crumb mull and under relatively comparable conditions. Two pairs of localities were selected for the purpose, all included in earlier studies.

Three of the places of study have been previously described (52, appendix, localities 1:A-B, and 10). The fourth is a woodlot with very typical crumb mull near Camillus, New York (52, table VII, samples 122 and 204 a-b). This was used for comparison with the Baldwinsville locality (No. 10). Unfortunately, the crumb mull locality 1:A at Jacksonville had soon to be abandoned, because the owner would not permit further access to his woodlot. Thus the comparison between the two woods at Jacksonville, which would have been particularly interesting, could not be carried out as planned. Instead, a woodlot with mull near Enfield (52, table VII, sample 209b) was chosen for comparison with the root duff locality 1:B at Jacksonville. Unfortunately, the series of determinations could not be made as long as would have been desirable, particularly not for the Baldwinsville-Camillus set.

As a first approach to the problem, nitrate tests were made in the spring on plants of the ground vegetation from crumb mull and root duff at Jacksonville. Such tests give a certain idea of the nitrate level of the soil in which the plants grow, and have been used for this purpose by Hesselman (18), Raunkiaer (49) and others. The tests were made quantitatively using Blom and Treschow's (3) method of analysis.

For a significant comparison, a nitrate collecting species had to be found growing in both localities. It was believed that some of the violets would fulfil the requirements (52, p. 588, footnote). A closer examination showed the impossibility of finding any violets or other nitratophilous plants on undisturbed root duff under the closed stand (52, appendix, p. 29). An attempt was made, however, to pick the specimens as far away as possible from openings. On May 13, 1931, a supply of *Viola pubescens* was collected in this way from both localities. The entire plant except the subterranean parts was taken. Sterile and flowering specimens were kept apart, making four lots in all, each weighing about 5 gm. when oven-dry.

Analyses of portions taken from the dried, powdered, and thoroughly mixed material showed the following contents of nitrate-N in milligrams per gram of dry sample:

	JACKSONVILLE CRUMB MULL	JACKSONVILLE ROOT DUFF
Flowering violets	4	0
Sterile	4	0

The result agrees with what can be inferred from direct field observation on the flora, and indicates that the storage experiments do not give a true idea of the nitrate level in the two soils. The storage experiments in this case had shown about the same nitrifying power for the F-layer of the root duff as for the crumb mull, sometimes one, sometimes the other, giving the higher value (52, tables VII and IX).[13]

Next, parallel determinations were made of the nitrate content per liter of soil, of the soil respiration, and of organic matter content.

Soil samples were taken with Burger's (6) steel cylinders of 1 liter capacity, 10 cm. high. Nitrates were determined by the phenoldisulfonic method, applied as described previously (52). Soil respiration was determined by the accumulation method (cf. p. 175), using a much simpler apparatus than the author's previous (51) model. The bell, made of heavy galvanized sheet iron, was low and wide, only 10 cm. high, but with .2 sq. m. cross section. A stirring device was provided with two long, narrow wings which could be moved by a crank from the outside. The crank was slowly turned during the whole experiment. The CO_2 accumulation was determined on air samples of 60 ml. volume sucked out by mercury into sampling tubes of glass (with mercury traps instead of stopcocks). One sample was taken at the beginning, another at the end of the experiment; the CO_2 accumulation was determined by the difference. The analyses were made in the laboratory using either a Pettersson or a Haldane standard gas analysis apparatus. The 60-ml. sample was sufficient for a double analysis.

A somewhat radical innovation in the soil respiration technique was that the rim of the bell was not pressed down into the ground. The bell was just placed on the surface, and it was only made certain that there were no visible openings between the rim and the soil. Any such openings were filled from the outside by heaping up some surface material. It is believed that with the great area of the bell and the consequently better proportion between area and circumference, the error due to CO_2 escaping to the sides is small when the tests are short (they were made to run about 10 minutes). It is true that this assumption has not thus far been proved by actual tests. The procedure described was nevertheless adopted because it was considered essential to use a technique disturbing the natural conditions as little as possible. Because of the sparse ground vegetation in the spots tested, one could even refrain from cutting any plants. The few and small green plants sometimes found inside the area enclosed by the bell were left undisturbed. The tests were all carried out in the early afternoon, between 1 and 3 p.m., except for one test made at 4 p.m.[14] In computing the results, the barometric pressures read in Ithaca and Syracuse have been used, corrected for the difference in elevation.

[13] In table IX, samples 332 are by mistake dated July instead of June. Samples 331 and 332 were taken on the same day, just as were the following two and two on the same dates (345–346, ... 368–369).

[14] This is mentioned because a daily period in soil respiration has been found. It is true that according to Porkka's (45) results the period does not seem very pronounced in forest soils.

The result of the determinations of nitrate content and of soil respiration are assembled in table 2.

It is seen that the nitrate level in the crumb mulls averages about twice as high as in the root duff soils. Where there are any nitrates at all, the values are, even in the individual cases, higher for the crumb mull, except on the two days July 27 and 29, where, for unknown reasons, there was an inversion, both in Enfield-Jacksonville and Baldwinsville-Camillus. There is hardly anything in the meteorological data to account for this freak.

On the other hand, the values of soil respiration are much the same for crumb mull and root duff. When the variation is considered, there is no difference in the averages. The figures are somewhat low, compared to the majority of those previously recorded (table 1), but their absolute height should be left undiscussed until the technique used has been checked.

TABLE 2

Nitrates in top decimeter of soil and soil respiration

DATE	CONTENT OF NITRATE-N IN MGM. PER LITER SOIL		RESPIRATION GM. CO_2 PER SQ. M. PER HOUR		LOCALITIES
	Crumb mull	Root duff	Crumb mull	Root duff	
May 27	1.7	1.5	....	....	Jacksonville
July 1	2.4	0.3	0.24	0.41	Enfield-Jacksonville
13	1.0	0.25	0.24	0.18	Enfield-Jacksonville
20	1.8	0.0	....	....	Camillus-Baldwinsville
22	0.2	0.0	0.30	0.16	Enfield-Jacksonville
27	0.6	1.1	0.37	0.12	Camillus-Baldwinsville
29	0.0	0.7	0.14	0.19	Enfield-Jacksonville
August 1	0.0	0.0	0.24	0.12	Enfield-Jacksonville
6	0.0	0.0	0.24	0.17	Enfield-Jacksonville
12	0.0	0.0	....	....	Enfield-Jacksonville
14	Trace	0.0	0.30	0.32	Camillus-Baldwinsville
Averages	0.7	0.35	0.26	0.21	

The conclusion to be drawn from table 2 is that evidently about the same total decomposition plus root respiration was going on in the crumb mull and the root duff soils, but that at the same time the nitrate level was in general much higher in the mulls. The former fact is to be expected from the general similarity in the character of the stands, which probably produce much the same amount of litter and have about the same amount of roots.[15] The latter fact is in complete agreement with the character of the vegetation and with the nitrate tests on violets, reported in the foregoing. Still the conclusion is

[15] The *distribution* of the roots can have no influence on the respiration values (provided the regime established is not disturbed in making the determination), unless the respiration of deeper roots should be depressed by lack of oxygen or excess of CO_2. This can not be expected to be common in normally drained soils (50).

not permissible that we here have proof that the two types of humus layer are different not in rate, but merely in type of decomposition (cf. the discussion in the preceding section). In order to obtain eventually such proof, the humus contents of the different soils must be considered.

Determinations of organic matter were made on all the 1-liter samples used for the nitrate tests, and in addition on some liter samples taken at greater depths down to 40 cm. The determinations were made by igniting at 550°C. the samples previously dried in a vacuum oven. The determinations include all organic matter present in the samples, whether living or dead (litter, humus, roots). In Enfield, no samples from greater depths could be taken because of the great number of stones in the soil. The results of the determinations on the first decimeter are, in kilograms per hectoliter, i.e. per square meter down to 10 cm. depth:

	ENFIELD-JACKSONVILLE	CAMILLUS-BALDWINSVILLE	MEAN
			kgm. per hl.
Crumb mull	10.6 ±2.0	10.3 ±0.47	10.5 ±1.05
Root duff	6.7 ±0.48	6.5 ±1.0	6.6 ±0.53

The somewhat surprising result is that *the root duff localities average distinctly lower*[16] *than those with crumb mull.* The determinations from greater depths did not reverse the picture. The results are, in kilograms per hectoliter:

DEPTH	CRUMB MULL PROFILE—CAMILLUS	ROOT DUFF PROFILES	
		Baldwinsville	Jacksonville
cm.			
10–20	8.8	3.8	4.3
20–30	7.2	2.0	4.1
30–40	5.8	2.0	Not determined

This gives the following totals down to 40 cm. depth for the two completely examined profiles at Camillus and Baldwinsville:

Crumb mull profile 32.1 kgm. organic matter per square meter
Root duff profile 14.3 kgm. organic matter per square meter

These figures seem to furnish conclusive proof that in the cases examined the distinctive difference between the two types of humus layer, the crumb mull and the root duff, is not at all in rate of decomposition. Better expressed, the difference is not in the direction which would be expected from current ideas. Under what can be confidently assumed to be very much the same conditions of litter-fall, the root duff has been found to represent a distinctly *lower* accumulation of organic matter than the crumb mull. If a conclusion as

[16] The difference of the means is 3.8 ± 1.17. The errors were computed as $\sqrt{\Sigma(d^2):n(n-1)}$.

to the rate of decomposition is permitted (cf. the discussion in a preceding section), it would be this: that the decomposition proceeds at a *faster* rate in the root duff than in the crumb mull.

At the same time, as shown in the foregoing, the nitrate level was found about twice as high in the crumb mull as in the root duff. Combined, these data seem to permit only one conclusion: that *the essential difference of crumb mull and root duff with respect to decomposition is in the course it takes, not in its rapidity.*

It might be useful to point out that even when referred to weight of organic matter the nitrate content of the crumb mull averaged higher than the root duff (5.2 as against 3.1 mgm. per kilogram organic matter). It is likewise interesting to note that the soil respiration, when referred to unit weight of organic matter present in the top decimeter of the soil, is twice as high in the root duff as it is in the crumb mull (32 mgm. as against 15 mgm. per kilogram organic matter and per hour). These figures seem to be conclusive.

The foregoing findings seem to furnish for the first time proof of the correctness of P. E. Müller's original view, against modern ideas (cf. the historical introduction) and seem to have rather far-reaching consequences, which will be discussed in the following parts of the paper. For the time being, the result stands alone, but data brought together in a preceding section strongly indicate the possibility of this being simply due to the fact that no such analysis has been attempted as has been made in the case just presented. In a way, of course, it can be said that the case analyzed is extreme. The root duff is a particularly light form of duff. Probably there are not many duff forms representing a considerably more rapid decomposition than the crumb mull. This does not make the present findings less interesting. What is important is the proof furnished against the general interpretation of duff formation as implying a slow decomposition, as compared to the supposedly very rapid breaking down of the organic matter in a good crumb mull.

It might be objected that this interpretation of the results is not independent of where the line is drawn between mull and duff. To a certain extent this is true. If the root duff had been included in the mull group, the conclusion drawn in the preceding paragraph would have had to be worded differently. But it should be pointed out that independently of any subtleties of classification there are striking differences, between the places examined, in litter cover and in development of the humus layer. In the mull localities, the litter is very scarce during most of the year, and never includes leaves older than 1 year. An unincorporated humus is totally lacking. In the root duff localities, the litter and F-layer include "little decomposed" remains of several years of litter-fall, and there is a distinct accumulation of unincorporated humus, strongly matted together by roots. These differences are among those generally prevailing between a good crumb mull and a duff. They are currently taken to imply or to prove a more rapid decomposition in the crumb mull type. The present comparative study has conclusively shown that this inference is not correct. It has been demonstrated that the rate of decomposition can

actually be as rapid as in the good crumb mull, or even more so, also where an unincorporated humus is formed and where several years of litter-fall are present in recognizable form. This important result stands independently of any possible controversies on classification.

With regard to the question of the "sampling effect," from which the experimental part of this study started, the results are not conclusive. The low amount of organic matter in the root duff, in particular of the F-layer, which is the chief carrier of the nitrifying activity, the small number of determinations and the great variation in actual nitrate content and nitrification during storage do not permit any definite conclusion. For this reason, the "sampling effect" is better discussed in a following part of the paper, where the question will be attacked from more general points of view.

SUMMARY

P. E. Müller's original view of the two main types of forest humus layer (mull and duff) being different in *type* of decomposition rather than in *rate*, is contrasted to modern ideas which consider the duff formation essentially as a result of a stagnation of the decomposing processes. An analysis of data brought together from the literature seems to show that the latter view is a result of optical and numerical illusions. The humus accumulation in duff layers has been overrated, probably mainly because so few determinations of their volume-weight or their humus content per unit volume have been made. Some such determinations from heavy duffs in the Adirondacks are reported. They agree very well with Vater's results from Germany. The total organic matter content of some European type profiles is computed. It appears that typical brown forest soil profiles with crumb mull may represent just as high a humus accumulation as podzol profiles with a heavy duff. Figures recently reported by Morgan and Lunt from this country lead to the same conclusion. An Adirondack profile with excessively heavy duff is computed and it is shown that not even such a great accumulation necessarily implies any "practical standstill of decomposition," as a heavy duff formation has frequently been interpreted.

The material available on "respiration" determinations on forests soils is critically reviewed, and some widespread errors are corrected. It is shown that soil respiration determinations do not necessarily show anything about the rate of decomposition. Under balanced natural conditions the carbon given off as carbon dioxide (plus what is removed by leaching) will correspond to the carbon contained in the litter-fall plus the amount given off by the roots. This will apply whether the decomposition is rapid or slow. The total organic matter accumulation, on the other hand, must be in inverse measure to the decomposition rate, under balanced and otherwise comparable conditions. Ramann's error of judgment on this point is criticized.

A comparison of two pairs of localities with root duff and crumb mull in the Finger Lakes region of New York State has given conclusive proof of these types of humus layer being distinguished by the course which the decomposition processes take, and not by a simple difference in their rapidity. This conclu-

sion is arrived at by determinations of nitrate level, soil respiration, and amount of organic matter down to 40 cm. depth. The respiration was the same for both types; a result to be expected from the close similarity in the character of the stand. The nitrate level averaged twice as high in the crumb mull as in the root duff, but the amount of organic matter was also much higher in the crumb mull profile, meaning that the rapidity of decomposition at least cannot well be higher than in the root duff. With equal soil respiration and different amounts of organic matter, it is evident that the respiration per unit weight of the latter must be different. In fact, it was twice as high in the root duff as in the crumb mull, whereas the nitrate content remained higher for the crumb mull even if referred to unit weight of organic matter. Thus, the higher nitrate level in the crumb mull cannot be accounted for by a more rapid decomposition. The difference is the other way.

The result seems to dispose of several current ideas. It shows that the presence of "little decomposed" remains of several years of litter-fall and the formation of an unincorporated humus do not necessarily imply a slow decomposition, as compared to a good crumb mull condition.

The conclusions drawn will be discussed further in the next part of the paper, to be published in a later issue.

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COMPARATIVE RATE OF DECOMPOSITION OF COMPOSTED MANURE AND SPENT MUSHROOM SOIL[1]

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In the study of the decomposition of composted horse manure by the cultivated mushroom, *Psalliota* (*Agaricus*) *campestris*, it was found that this organism feeds primarily upon the lignins and the proteins of the composts and only to a less extent upon the hemicelluloses and the cellulose (4). This process of nutrition is just the opposite from that of the common fungi and bacteria living in the soil and in composts. In the composting of stable manure, as well as in the decomposition of plant and animal residues in the soil, the microörganisms, including numerous fungi and bacteria, attack—next to the sugars, starches, and proteins—the hemicelluloses and the cellulose; these are reduced in relative concentration more rapidly than the organic matter as a whole. The lignins are more resistant to attack by the microörganisms of composts and soils, and will, therefore, accumulate. In the decomposing plant residues, low in nitrogen, the proteins will accumulate, since they are continuously synthesized in the form of cell substance of microörganisms. When such a compost of horse manure was used for the growth of the cultivated mushroom, it was found (3) that this growth was accompanied not only by a marked decrease in the lignins and in the proteins of the compost, but also by a marked increase of the water-soluble substances, especially the nitrogenous complexes. It was suggested that the first is due to the feeding of the mushroom upon the lignins and the proteins and the second to the synthesis of estensive mushroom mycelium, which penetrates through the compost and a large part of which is water soluble.

In view of the fact that the resistance to decomposition of the organic nitrogenous complexes in composts and in soil is due to their combination with the lignins of the plant residues, to form resistant complexes (2), one would expect that any organism capable of attacking such complexes, as seems to be the case of the mushroom fungus, would bring about the transformation of the nitrogen into a form in which it would become more readily available to the common fungi and bacteria of the soil. As a correlary of these observations, one would expect that composted manure should decompose in the soil much

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more readily after the mushroom fungus has grown upon it than before, and the nitrogen should be liberated more readily in an available form.

In this connection it may be of interest to call attention to the results obtained by Falck (1), who found that tree residues, which have been decomposed by a fungus attacking primarily the lignins will, after such decomposition, be readily attacked by other organisms, whereas the same residues which were first acted upon by organisms attacking the cellulose and not the lignin will not be decomposed later by the lignin-decomposing fungus; in other words, the growth of lignin-decomposing organisms makes the residues more readily decomposed by the common microbial flora of the soil, whereas the growth of cellulose-decomposing organisms makes the residue more resistant to decomposition.

TABLE 1

Chemical composition of fresh and composted horse manure before and after the growth of* Agaricus campestris

Per cent of dry matter

NATURE OF MATERIAL	FRESH MANURE		COMPOSTED MANURE		
	Control	*Agaricus*	Control	*Agaricus* I	*Agaricus* II
Ether-soluble portion	2.46	1.08	1.26	0.48	0.43
Water-soluble organic matter	6.31	34.22	3.24	18.70	25.05
Hemicelluloses	18.10	5.50	6.80	2.64	2.02
Cellulose	21.40	9.70	12.51	7.51	6.66
Lignin	21.30	11.00	22.91	7.77	6.31
Ash	16.90	29.10	45.20	56.90	61.50
Total nitrogen	1.18	2.71	1.56	1.77	1.79
Water-soluble nitrogen	0.32	1.08	0.14	0.88	0.17
Ammonia-N	0.06	0.32	0.04	0.28	0.47

* 237 days on fresh manure and 215 days on composted manure.

In order to determine how far these principles apply to the growth of the mushroom fungus, which attacks the lignins, in rendering the residual compost a more readily available source of energy for the common fungi and bacteria of the soil, quantities of fresh and composted horse manure were washed with water to remove most of the water-soluble constituents, placed in bottles, sterilized, and inoculated with pure culture spawn of the mushroom. The bottles were incubated for 215 days, then were broken and the material was removed for analysis (table 1). Two-gram portions, on a dry basis, of the fresh and composted manure which had been kept in a sterile condition in bottles, as well as 2-gm. portions of the fresh and composted manure which had been decomposed by the mushroom fungus, were added to a series of 100-gm. portions of fresh soil placed in flasks. The moisture content of the soil was adjusted to optimum for the growth of aerobic organisms and the flasks were connected with the respiration apparatus in the incubator, at 28°C. The amounts of

CO_2 given off daily in the process of decomposition of the various preparations were determined (fig. 1).

In a parallel experiment, 4-gm. portions of the composts were added to 100-gm. portions of the same soil and incubated for 6 weeks. The amount of

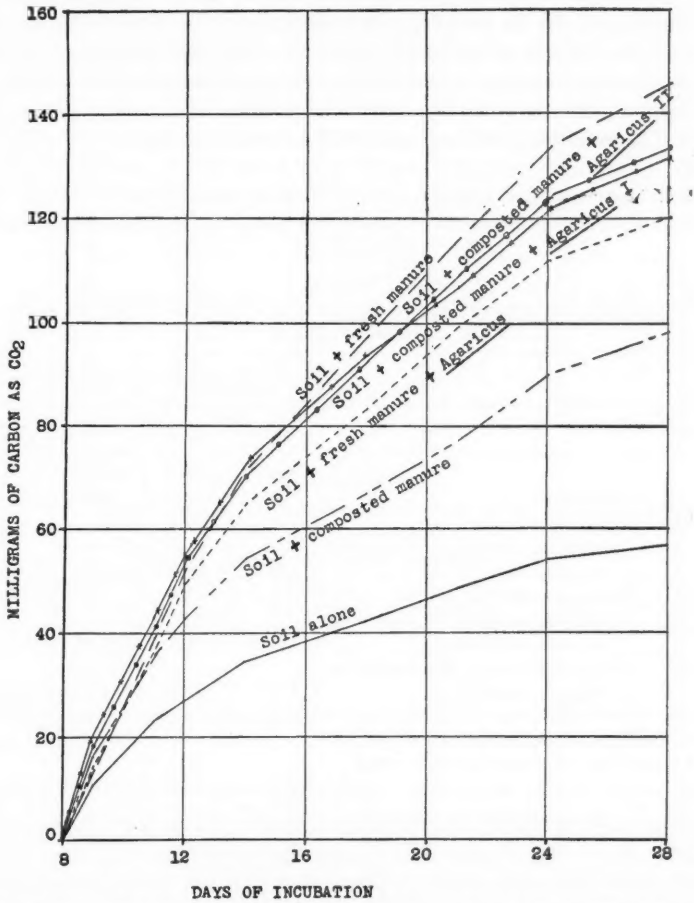

FIG. 1. RATE OF CO_2 EVOLUTION FROM 100-GM. PORTIONS OF SOIL TO WHICH WERE ADDED 2-GM. PORTIONS OF FRESH AND COMPOSTED MANURE, KEPT AS CONTROLS OR IN WHICH THE CULTIVATED MUSHROOM *Agaricus campestris* HAS GROWN FOR 216 DAYS

nitrate produced at the end of that period was determined (table 2). Both sets of results show that in the case of fresh, uncomposted manure, less CO_2 was given off from the sample acted upon by the mushroom fungus and more nitrate was produced than from the corresponding manure in which the mush-

room fungus did not grow but was kept as control. This can be readily understood: fresh manure is rich in readily decomposable carbohydrates, such as hemicelluloses and cellulose, but is low in total nitrogen; as a result of this the rapid decomposition of the carbohydrates, as shown by the CO_2 liberation, is not accompanied by nitrogen liberation, since whatever nitrogen might be liberated is used by the microörganisms for the synthesis of microbial cell substance. In the case of the same manure in which the mushroom was previously grown, there is a reduction of carbohydrates and a marked increase in nitrogen content, especially the water-soluble form; this is responsible for the lower CO_2 evolution in soil and greater liberation of nitrogen in an available form.

With the composted manure, totally different results were obtained. The manure itself was decomposed in the soil to a less extent than the corresponding

TABLE 2

Influence of Agaricus campestris *upon making the organic complexes in composts available to soil microörganisms*

NUMBER	NATURE OF COMPOST ADDED TO SOIL	CARBON DIOXIDE LIBERATED*		NITRATE FORMED†	
		Total	Above control	Total	Above control
		mgm. C	*mgm. C*	*mgm. N*	*mgm. N*
1	Control soil	57.3	.....	0.97	.....
2	Fresh manure, control	146.0	88.7	0	−0.97
3	Fresh manure, decomposed by *Agaricus campestris*	120.9	63.6	13.75	+12.78
4	Composted manure, control	98.2	40.9	1.42	+0.05
5	Composted manure, decomposed by *Agaricus campestris* I	132.0	74.7	10.55	+9.58
6	Composted manure, decomposed by *Agaricus campestris* II	134.1	76.8	11.45	+10.48

* From 2 gm. of preparations in 20 days.

† From 4 gm. of preparations in 6 weeks.

fresh manure, because in the composted manure there was a reduction of the readily decomposable substances during the process of composting. As a result of decomposition of the composted manure in soil, there was no nitrogen consumed, but a small amount was actually liberated in an available form, as a result of the much narrower carbon: nitrogen ratio in the composted than in the fresh manure. However, when the composted manure was previously used as a medium for the growth of the mushroom fungus it decomposed much more readily in the soil, as shown by the increased CO_2 evolution and especially by the considerably greater liberation of the nitrogen in an available form. These results prove definitely that composted manure in which the mushroom fungus has been grown, namely the so-called spent mushroom soil, will decom-

pose faster and allow a more rapid liberation of the nitrogen in an available form, but will probably leave much smaller quantities of organic residues in the soil; in other words, spent mushroom soil should be preferable to composted manure as a source of plant nutrients, whereas as a source of humus it should be of inferior value, since it disappears more rapidly than composted manure.

In order to determine what effect the growth of the mushroom fungus has upon the decomposition of other humus complexes, in which an enrichment in lignin and protein has taken place, lowmoor peat was used as a medium. Two-hundred-fifty-gram portions of a lowmoor peat from New Jersey, containing about 50 to 52 per cent moisture, were placed in bottles and sterilized under pressure. Some of the bottles were left as controls and some were inoculated

TABLE 3

Decomposition of lowmoor peat by Agaricus campestris

TREATMENT OF PEAT	TOTAL MATERIAL LEFT	TOTAL WATER-SOLUBLE MATERIAL	TOTAL WATER-SOLUBLE NITROGEN	AMMONIA NITROGEN
	gm.	*mgm.*	*mgm.*	*mgm.*
Sterilized, control peat	128.6	1.717	84.2	38.9
Peat in which *Ag. campestris* was grown for 60 days	120.5	3.221	142.0	61.9

TABLE 4

Influence of the growth of Agaricus campestris *upon the availability of the organic complexes in lowmoor peat to soil microörganisms*

On basis of 30 gm. of dry peat decomposed for 17 days

NATURE OF PEAT	CO_2 LIBERATED	TOTAL WATER-SOLUBLE MATERIAL	TOTAL WATER-SOLUBLE NITROGEN
	mgm. C	*mgm.*	*mgm.*
Control peat	68.3	277	9.6
Peat in which *Ag. campestris* was grown	107.4	728	32.2

with the spawn of the mushroom fungus. A very fine extensive mycelium of the fungus was produced through the peat, far less abundant than in the case of the composted and even fresh manure used as a medium. After 60 days' incubation, the culture material was removed from the bottles and analyzed (table 3). The results show that as a result of the growth of the mushroom fungus on peat, there was a reduction in the total dry material, accompanied by an increase in water-soluble substances, including nitrogen compounds.

Both the peat kept as control and the peat in which the fungus was grown were now subjected to decomposition by the common microbial flora and fauna of the soil. Fifty-gram portions of the various air-dry peat preparations were placed in flasks, 75-cc. portions of water added, and all the flasks inoculated with a fresh soil infusion. The amount of CO_2 given off during a period of 17

days was measured and, at the end of that period, the water-soluble organic matter, the total nitrogen, and the ammonia nitrogen were determined in the peat cultures (table 4).

As a result of the growth of the mushroom fungus, the peat was rendered more readily decomposable by the common fungi and bacteria of the soil. This is clearly seen by the increase in evolution of CO_2 and the increase in the solubility of the nitrogen in the peat. This peat is high in nitrogen (about 3 per cent on a dry basis), but the nitrogen is not made readily available as a result of its decomposition by the common microbial population of the soil. However, when the *Agaricus* was grown upon the peat, it produced certain changes in the chemical relation of the organic complexes, which rendered the nitrogen more readily available to the common soil fungi and bacteria.

It was of interest to determine whether the growth of the common mushroom upon composted manure results in a change in the chemical nature of the humus complexes, besides reducing the lignins and rendering the proteins

TABLE 5

Influence of Agaricus campestris *upon the solubility of the humus in composted manure*

MATERIAL	SOLUBLE IN COLD NaOH SOLUTION AND PRECIPITATED BY HCl		SOLUBLE IN HOT NaOH SOLUTION (AFTER COLD) AND PRECIPITATED BY HCl	
	Yield	Nitrogen content of precipitate	Yield	Nitrogen content of precipitate
	per cent	*per cent*	*per cent*	*per cent*
Control	4.24	3.37	11.41	3.24
Ag. campestris I	9.50	4.00	4.93	2.88
Ag. campestris II	9.01	4.30	5.28	3.28

more soluble. The composted manure used in the first experiment, without and with the growth of the *Agaricus campestris*, was treated for 24 hours in the cold with 4 per cent NaOH solution. The extract was removed by filtration and was acidified in the cold with HCl; the precipitate was filtered off, washed free from chlorides, dried, weighed, and analyzed for total nitrogen. The residue left after the cold extraction with NaOH was now extracted with fresh 4 per cent NaOH solution for 1 hour at 15 pounds' pressure. The second extract was also removed by filtration, acidified with HCl, and the precipitate washed and dried. Table 5 shows that as a result of the growth of *Agaricus campestris* upon composted horse manure, there is a definite change in the chemical nature of the humus, as shown by a marked increase in the fraction soluble in cold NaOH solution and the nitrogen content of the precipitated material ("humic acid"): actually three times as much of the nitrogenous complexes were rendered soluble by cold alkali-solutions as a result of the growth of the mushroom fungus upon the composted manure. The fact that this is not due to an increase of this part of the humus at the expense of the

other organic complexes of the compost is shown by the reduction in the fraction soluble in hot alkali solution following the cold. As a result of the growth of the mushroom the humus of the compost was rendered more readily soluble in cold alkali solution.

SUMMARY

The growth of the cultivated mushroom, *Agaricus campestris*, upon composted manure results in rendering the organic complexes more readily decomposable by the microbial population of the soil.

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FURTHER STUDIES ON THE VALUE OF VARIOUS TYPES OF ORGANIC MATTER FOR IMPROVING THE PHYSICAL CONDITION OF SOILS FOR PLANT GROWTH[1]

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Investigations reported previously (3) have shown that three widely different classes of soils were markedly improved for plant growth by the incorporation of various types of organic materials. The improvement obtained from organic additions was largely due to changes in the physical properties of the soils rather than to the nutrients supplied.

Since the experiments on which these conclusions rest were conducted under a system of limited watering, equivalent to about 2 inches of rainfall a month, the results were considered not strictly applicable to conditions of more abundant moisture supply, particularly for clay loam soils having a strong tendency toward unfavorable compaction. Likewise, the questions of the relative persistence of the various types of organic matter in the soil after incorporation, and the changes occurring in the moisture holding capacities of the various organic materials upon drying required further elucidation. Studies of these problems have been made and are here presented.

IMPROVING THE PHYSICAL PROPERTIES OF A CLAY LOAM SOIL

A critical experiment was conducted during the winter of 1930–31 to determine the relative values of five types of organic substances for improving the physical condition of a clay loam soil, under a system of abundant watering. The soil was practically identical with that used in former studies, having a pH of 5.93, a loss on ignition of 6.5 per cent, a hygroscopic coefficient of 7.2 per cent, a maximum water holding capacity of 36.2 per cent, and an available water holding capacity of 25.7 per cent. The properties of the five types of organic matter have been noted elsewhere (3).

The method of procedure was that followed in former tests, except in the amount of water supplied. In this series of pots (9-inch clay flower pots), 740 cc. of water was added weekly (equivalent to 4 inches of rainfall monthly) to each culture from December 16, after the grass seed had germinated, until

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January 5. The amount was then increased to 1,210 cc. weekly until February 5, to 2,490 cc. until March 3, and to 4,980 cc. until harvest on April 2. The total moisture supplied during this period was equivalent to about six times the quantity used in the previous experiments.

As a result of the more liberal supply of moisture the yields of dried grass were 22 gm. for the untreated soil as compared with 9.6 gm. produced with this soil under a limited system of watering in 1929–30. In spite of losses by percolation, the grass plants showed no signs of wilting in the present experiment, whereas wilting frequently occurred with moisture limited to 2 inches monthly.

The mean daily temperature for the entire growth period was 66°F., and the mean daily water loss from a Livingston atmometer, 105 cc. These values are approximately the same as those noted in the series grown in 1929–30, and are not greatly different from those experienced in the field for the growing season. In general, it may be said that the atmospheric conditions were fully as favorable for the growth of grass as those encountered during the normal growing season of the region.

Experimental results

The effect of incorporating various types of organic matter on the physical properties of the clay loam soils and upon plant growth is shown in table 1. It is noteworthy that the abundant watering produced a satisfactory growth of grass with all treatments, including soil which had received no organic matter. Although the soil was packed firmly in the pots at the time of filling, the drainage was adequate at all times during the experiment, since the plant roots occupied the entire soil mass before compaction from watering had progressed sufficiently to hamper percolation.

An important result was the general increase in plant growth from the use of all five types of organic matter. Furthermore, increasing the amount of organic substance from 73.5 gm. to 147 gm. for every 3,900 gm. of soil, caused nearly as great additional improvement in plant growth as the initial application. With a limited moisture supply, it was observed previously that increasing the quantity of peats reduced plant growth, particularly in the case of imported peat moss. In these instances, reduced growth occurred in spite of improvement in the physical properties of the soil, because of the excessive moisture losses from evaporation and percolation.

The various types of organic matter with abundant moisture respond quite differently from those with limited moisture. Instead of the moderately fibrous Michigan peat showing a distinct advantage over the granular cultivated New Jersey peat, the two substances permitted approximately equal growth with abundant watering. The tardy absorption of water noted for peat moss under conditions of limited moisture supply did not retard plant growth when the moisture supply was abundant.

The relatively high yields of grass on soils receiving spent mushroom soil and manure must be attributed in part to the plant nutrients contained by

these substances. Although sulfate of ammonia was applied periodically during the experiment, this fertilization did not completely overcome the initial differences in nutrient supplying power of the various soil mixtures.

TABLE 1

The effect of different types of organic matter additions on the physical properties of a clay loam soil, and on yields of grass produced, with abundant watering

TYPE OF MATERIAL ADDED TO THE SOIL	IGNITION LOSS			AVAILABLE WATER HOLDING CAPACITY*		PORE SPACE† OF SOILS AFTER GROWTH OF GRASS		PERCOLATION OF WATER IN 30 MINUTES	GRASS YIELDS PER POT (DRY WEIGHTS OF TOPS)
	Before growth of grass	After growth of grass	Proportion lost	Before growth of grass	After growth of grass	Actual	Difference from check		
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*gm.*
A. Light additions of organic matter—73.5 gm. dry matter to 3,900 gm. moisture-free soil									
Cultivated N. J. peat	7.6	7.2	5.3	30.2	29.7	54.6	+0.1	112	24.7
Raw Michigan peat	7.8	6.9	11.5	27.2	27.7	56.1	+1.6	105	24.1
Imported peat moss	7.8	6.2	20.5	34.1	31.0	61.4	+6.9	121	26.0
Spent mushroom soil	6.8	6.1	10.3	26.0	25.3	53.5	−1.0	94	24.7
Well-rotted manure	7.2	6.2	13.9	27.2	27.9	55.7	+1.2	100	27.7
B. Heavy additions of organic matter—147 gm. dry matter to 3,900 gm. moisture-free soil									
Cultivated N. J. peat	8.8	8.5	3.4	33.9	31.1	57.1	+2.6	167	26.2
Raw Michigan peat	8.0	7.2	10.0	30.5	29.4	56.2	+1.8	135	26.3
Imported peat moss	9.1	8.2	9.9	39.9	40.2	64.6	+10.1	128	27.5
Spent mushroom soil	7.0	6.4	8.6	28.8	25.4	52.3	−2.2	90	27.4
Well-rotted manure	8.2	7.1	13.4	34.0	27.4	56.8	+2.3	129	29.5
C. Average of both light and heavy additions of organic matter									
Cultivated N. J. peat	8.20	7.85	4.3	32.0	30.4	55.9	+1.4	140	25.5
Raw Michigan peat	7.90	7.05	10.8	28.8	28.5	56.2	+1.7	120	25.2
Imported peat moss	8.45	7.20	14.8	37.0	35.6	63.0	+8.5	125	26.8
Spent mushroom soil	6.90	6.25	9.4	27.4	25.4	52.9	−1.6	92	26.0
Well-rotted manure	7.70	6.65	13.6	30.6	27.7	56.3	+1.8	115	28.6
Check (no organic matter added)	6.5	6.2	4.9	25.7	26.2	54.5	....	107	22.0

* Available water holding capacity determined by subtracting the wilting coefficient (indirectly determined from hygroscopic coefficient) from the maximum water holding capacity (1).

† Pore space determined with aid of Lebedeff soil sampling tube (2).

Support of this statement is found in the physical properties of the soil mixtures, those containing spent mushroom soil and manure being inferior to those containing some form of peat.

Since the temporary physical effects of organic matter additions to soil are relatively unimportant as compared with the more permanent effects, attention may be centered on the available water holding capacities of soil-organic matter mixtures *after* the growth of grass for the equivalent of a normal season. The improvement in this property is due in part to the incorporation of organic matter with its relatively high water holding capacity, and in part to the improvement in soil structure produced by the presence of organic matter and the effect of the grass roots. Mushroom soil had no lasting beneficial effect on structure because of its relatively low organic matter content (about 24 per cent) combined with rapid decomposition and high soil content. Peat moss proved most effective in raising the moisture holding capacity, followed in order by cultivated New Jersey peat, raw peat from Michigan, and manure.

With regard to pore space, spent mushroom soil was the only material that failed to increase this property of the soil when incorporated therein. Peat moss was the most potent in improving pore space of the clay loam, manure and raw peat followed in degree of effectiveness, with cultivated New Jersey peat nearly as valuable.

Since relatively small changes in total pore space may be accompanied by important changes in structure and differences in water and air movements within the soil mass, rates of percolation for water were determined in the manner described in the previous studies. Cultivated New Jersey peat proved the most valuable substance for increasing the removal of excess water from the soil; peat moss, raw Michigan peat, and manure ranked in order of importance as listed. The spent mushroom soil actually reduced percolation rates.

Determinations of loss on ignition were made as a measure of the relative persistence of the various types of organic matter in the soil. Obviously, the beneficial physical effects of incorporating such substances with soil will continue as long as they are present, and will disappear shortly after the organic content of the soil falls to its former level. The persistence of any organic material is determined by the speed with which it decays after being mixed with the soil. Types of organic matter, such as cultivated peat, that have reached an advanced stage of decay are considerably more resistant to further decomposition than raw peat and peat moss, which have a higher percentage content of readily decomposable compounds. In this connection, it should be recalled that the resistance to decay of the pure substances, is quite different from that exhibited when mixed with soil or fertilizer materials.

Of the five organic matter types tested, cultivated New Jersey peat showed greatest resistance to decay when incorporated with the soil and cropped to grass. Raw Michigan peat disappeared more than twice as rapidly and peat moss three to four times as rapidly as cultivated peat. Well-rotted manure decomposed more readily than raw peat, and less than peat moss. Considering the fact that only one-fourth of the dry matter in mushroom soil was organic in nature, the loss during the growth period of 16 weeks was even greater than for well-rotted manure.

From the standpoint of the persistence of the various types of organic matter, their respective effects on the physical properties of the soil, and the plant growth obtained, the conclusion may be drawn that cultivated New Jersey peat is the most valuable of these types for improving the physical properties of well-watered clay loam soils. Raw peat ranks next in value, followed in order by peat moss, well-rotted manure, and spent mushroom soil. These results are quite different from those obtained with the same material and soil under a limited moisture supply, in which moderately fibrous materials, such as raw peat and manure, were apparently superior.

The application of the results here reported, to field conditions should be made with certain qualifications. Clay loam soils in the eastern United States in many cases are underlaid by a layer of compact soil which may impede subdrainage. The incorporation of organic matter with the surface layers of soil will not correct faulty structure in lower horizons. In locations where drainage is adequate, the relative value of various types of organic matter for improving the physical properties of the soil for plant growth should be approximately as determined in this experiment. Nutrient deficiencies should be corrected, however, and adequate moisture must be provided for satisfactory results, particularly during the first season of growth after incorporation of the organic matter.

EFFECT OF DRYING VARIOUS TYPES OF ORGANIC MATTER UPON THEIR ABILITY TO ABSORB MOISTURE

One of the practical difficulties involving the use of peaty materials for soil improvement is their peculiar relation to water absorption. Although they are recognized as having high absorptive capacities for moisture, layers of these organic substances placed at or below the surface of the soil have appeared to repel water, either allowing moisture to pass through without retention, or restricting water movement and even shedding water as though oiled. A preliminary study of the phenomenon suggested that the explanation lay in the effect of drying on the content of colloidal matter.

An experiment was conducted to determine whether the various peaty substances behaved in the same manner upon drying, or whether they differed greatly in the speed with which the initial water capacity was recovered after being dried and in the extent to which the drying produced an irreversible reaction. In the first tests, the materials were treated in two ways. After being thoroughly mixed, each lot was divided into two equal parts (three for Michigan peat); one part was thoroughly dried in the greenhouse and the other was maintained at its natural moisture content. The peat moss, being obtained in a very dry condition, was divided into two similar lots and one of these was soaked for several days to increase its water content.

All of the materials were then carefully packed into 9-inch flower pots and water was added in equal amounts to each lot of organic matter. The quantity used was equivalent to the calculated maximum water holding capacity of the most absorbent material, namely, peat moss. This amounted to 10.35

kgm. of water for each 1,000 gm. (dry basis) of each type of organic matter. The water was applied as rapidly as it entered the organic matter, and the excess was allowed to drain off. The water content of each substance was then determined, following which an additional application of water was made. After a second analysis, a third addition of water was supplied and a third analysis for moisture content made. The detailed results are given in table 2.

In every instance, drying had an adverse effect on the water holding capacity, even after several times as much water had been added as would completely saturate each substance. In the case of cultivated New Jersey peat,

TABLE 2

Effect of drying various types of organic matter upon their ability to absorb moisture, when equal amounts of water are applied to all materials

TYPE OF ORGANIC MATTER TESTED	PREVIOUS TREATMENT	APPROXIMATE MOISTURE CONTENT WHEN TESTED (DRY-BASIS)	WATER ADDED IN EACH ADDITION PER 1,000 GM. OF DRY MATTER	MOISTURE HELD AFTER EACH SUCCESSIVE APPLICATION* OF WATER (DRY-BASIS)			RELATIVE AMOUNTS OF WATER HELD AFTER THIRD ADDITION
				After first addition	After second addition	After third addition	
		per cent	*kgm.*	*per cent*	*per cent*	*per cent*	*per cent*
Cultivated N. J. peat	Natural moisture content	180	10.35	257	282	287	100.0
	Dried in greenhouse	12	10.35	213	243	248	86.4
Raw N. J. peat	Natural moisture content	180	10.35	372	410	439	100.0
	Dried in greenhouse	12	10.35	262	298	308	70.2
Raw Michigan peat	Natural moisture content	150	10.35	241	254	285	100.0
	Dried in greenhouse	12	10.35	147	217	227	79.7
	Dried in oven	...	10.35	75	170	201	70.5
Imported peat moss	Soaked several days	670	10.35	920	953	1137	100.0
	Dried in greenhouse	14	10.35	135	453	600	52.8

* Equal amounts of water were added to all lots of organic matter, the quantity used for each addition being equivalent to the calculated maximum water holding capacity of the most absorbent material, namely, peat moss.

drying proved least harmful; nevertheless, only 86.4 per cent of the water holding capacity was regained by three successive additions of water. Raw New Jersey peat from the same deposit showed a much lower recovery of absorptive power than the cultivated peat. Raw Michigen peat had a recovery of 79.7 per cent after drying in the greenhouse, as compared with 70.5 per cent following oven-drying. The oven-dried peat was nearly free of moisture at the beginning of the experiment, but the actual water content was not determined. The peat moss lost very little water upon further drying in the greenhouse because its moisture content was already very low. The addition

of three times its theoretical water capacity to each of the two lots of peat moss only succeeded in restoring 52.8 per cent of the capacity exhibited by material after soaking several days.

An additional test on the effect of drying the several types of organic matter was conducted to determine their relative capacities for absorption. In this case, the quantity of moisture added to each material was equivalent to its respective water holding capacity. Three lots of each material were pre-

TABLE 3

Effect of drying various types of organic matter upon their ability to absorb water when the water added is proportional to the maximum water holding capacities of the respective materials

TYPE OF ORGANIC MATTER TESTED	PREVIOUS TREATMENT	MOISTURE CONTENT AT BEGINNING OF TEST (DRY-BASIS)	WATER ADDED IN EACH ADDITION PER 1,000 GM. OF DRY MATTER	WATER HELD AFTER EACH SUCCESSIVE APPLICATION OF WATER* (DRY-BASIS)			RELATIVE AMOUNTS OF WATER HELD AFTER THIRD ADDITION
				After first addition	After second addition	After third addition	
		per cent	*kgm.*	*per cent*	*per cent*	*per cent*	*per cent*
Cultivated N. J. peat	Natural moisture content	160	2.68	258	278	292	100.0
	Prolonged soaking in water	...	2.68	246	255	287	98.3
	Dried in greenhouse	13	2.68	172	237	247	84.6
Raw N. J. peat	Natural moisture content	294	4.39	493	...	510	100.0
	Prolonged soaking in water	464	4.39	502	507	509	99.8
	Dried in greenhouse	11	4.39	36	107	171	33.5
Raw Michigan peat	Natural moisture content	83	3.46	203	270	271	100.0
	Prolonged soaking in water	227	3.46	243	262	270	99.6
	Dried in greenhouse	11	3.46	29	76	200	73.9
Imported peat moss	Natural moisture content	18	10.35	101	439	528	59.1
	Prolonged soaking in water	...	10.35	821	863	894	100.0
	Dried in greenhouse	11	10.35	109	430	536	60.0

* The quantity of water added to each lot of organic matter for each addition was approximately equal to the theoretical maximum water holding capacities of the respective types of materials.

pared; one untreated, another soaked in water, and a third air-dried in the greenhouse for comparison with the behavior of the untreated material.

The data presented in table 3 indicate that prolonged soaking did not increase the water holding power of cultivated New Jersey peat, raw New Jersey peat, or raw Michigan peat. Imported peat moss, having a low initial moisture content, was greatly improved by soaking. Peat moss at the normal moisture content of 18 per cent recovered only 59.1 per cent of its potential capacity by three successive additions of the full calculated quantity of water

needed for complete saturation. Further air-drying in the greenhouse did not reduce the absorptive capacity below that of the untreated lot.

Drying produced the least effect on cultivated New Jersey peat, and the greatest on raw New Jersey peat. The behavior of the raw New Jersey peat was unusual in view of its performance noted in table 2. Nevertheless, it is clear that partially decomposed peat is less injured by drying than raw peat, since the cultivated product recovered 84.6 per cent of its water capacity, and raw Michigan peat recovered but 73.9 per cent, as a result of three successive additions of water. This performance was quite similar to that noted for the materials in the test reported in table 2.

In general it may be stated that all of the types of peat investigated were injured in absorptive capacity by drying. The critical moisture content, below which drying should not occur, has not been determined, but thorough air-drying obviously was detrimental. Under field conditions, the tardy absorption of water by dried peaty materials will doubtless greatly increase moisture losses by run-off where such materials are present in considerable quantities as a layer at the surface. Layers of peaty materials placed below the surface are less likely to suffer extreme drying, but may become desiccated in periods of drought. When dried, these layers may be expected to restrict water movement if compacted, and to cause excessive aeration if sufficiently porous to permit the passage of water. In either case the root activities of plants would be unfavorably affected.

PERSISTENCE OF FOUR SOURCES OF ORGANIC MATTER WHEN INCORPORATED WITH LOAM SOIL, IN THE FIELD

It is obvious that the value of any type of organic matter for improving the physical condition of soil is determined in part by its persistence upon incorporation with soil. Previous tests (3) conducted in the greenhouse indicated that the organic matter of cultivated peat was most resistant to decay. Raw Michigan peat decomposed more rapidly than cultivated peat but less rapidly than rotted manure. Imported peat moss, although slow to decay in the pure state, decomposed even more rapidly than manure when incorporated with mildly acid soil. When the actual quantity of organic substance present in spent mushroom soil is considered, the rate of decomposition was fully as rapid as that of well-rotted manure. All of these observations, however, were made with soil-organic matter mixtures cropped to grass in the greenhouse, and examined at the end of a period of about 4 months.

Field tests on the persistence of organic matter types were begun in September, 1929, on a well-drained, mildly acid, loam soil. The organic substances were well mixed with the upper 4 inches of soil in 10- by 10-foot plots. Each material was used at the rate of 168 pounds of dry matter per 1,000 square feet of surface in duplicate plots, and also at the rate of 336 pounds in adjoining plots. One untreated companion plot was provided for every set of two plots receiving organic matter additions.

The entire series of plots was planted to a mixture of lawn grasses in September, 1929, and a satisfactory stand of grass was obtained. During the season of 1930 the turf was fertilized with 15 pounds of an 8–6–4 fertilizer per

TABLE 4

Effect of incorporating various types of organic matter on the organic content of field soils planted to lawn grasses

TYPE OF ORGANIC MATTER INCORPORATED WITH THE SOIL BEFORE PLANTING*	LOSS ON IGNITION, FOR SOIL PLANTED TO GRASS IN SEPTEMBER, 1929						
	November, 1929		November, 1931		Difference between untreated soil in 1929, and treated soil in 1931	Difference between untreated soil in 1931, and treated soil in 1931	Increase from growth of grass only, 1929 to 1931
	Untreated soil†	Treated soil	Untreated soil†	Treated soil			
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Incorporated at rate of 168 pounds dry matter per 1,000 square feet of surface							
Cultivated N. J. peat	4.71	4.91	5.02	5.76	+24.4	+14.5	
Peat moss manure	4.73	....	5.09	5.06	+7.0	−0.6	
Spent mushroom soil	4.72	4.82	4.97	4.99	+5.7	+0.4	
Well-rotted manure	4.76	5.05	4.89	5.12	+7.6	+4.7	
Average					+11.2	+5.05	
Incorporated at rate of 336 pounds dry matter per 1,000 square feet of surface							
Cultivated N. J. peat	4.71	5.22	5.02	5.57	+18.2	+10.7	
Peat moss manure	4.73	....	5.09	5.62	+18.8	+10.0	
Spent mushroom soil	4.72	4.89	4.97	5.02	+6.4	+1.0	
Well-rotted manure	4.76	5.05	4.89	5.52	+15.9	+12.9	
Average					+14.8	+8.65	
Average for both rates							
Cultivated N. J. peat	4.71	5.06	5.02	5.66	+20.2	+12.7	+6.8
Peat moss manure	4.73	....	5.09	5.34	+12.9	+4.9	+7.6
Spent mushroom soil	4.72	4.85	4.97	5.00	+5.9	+0.6	+5.3
Well-rotted manure	4.76	5.05	4.89	5.32	+11.7	+8.8	+2.9
Average					+12.7	+6.75	+5.65

* The organic materials were mixed with the upper 4 inches of soil in every case.

† The untreated plots were companion plots for the respective treated plots in every instance.

1,000 square feet and in 1931 with 20 pounds. The plots were mowed regularly at a height of three-fourths inch, and watered occasionally during the unusual drought of 1930 to prevent injury to the sward.

Distinct differences in the density and vigor of the turf were noted for the several treatments throughout the two seasons of growth. In general, the most satisfactory development was made on plots receiving the heavy additions of organic matter. The incorporation of the lighter amounts of organic substances, however, permitted a more vigorous growth than that obtained on the untreated companion plots. No weights of grass clippings were obtained, so that quantitative measures of relative growth are not available.

Soil samples were drawn from the upper 4 inches of each plot in November, 1929, and again in November, 1931. Loss-on-ignition determinations were made on these samples as an index of the relative persistence of the various types of organic matter during the 2-year period. The data from duplicate plots were averaged, and the results are presented in table 4.

The outstanding difference between results in the field and those in the greenhouse tests was the fact that loss-on-ignition values displayed a consistent increase in the field plots, while the greenhouse soils showed significant decreases. The average loss on ignition for the eight untreated plots increased from 4.73 per cent to 4.99 per cent as a result of the occupation of the soil by grass roots. Plots receiving organic matter at the beginning of the experiment indicated still greater gains than the untreated companion plots. Presumably the larger increases in soil organic matter arose from greater growth of grass roots following improvement of the physical condition of the soil by the incorporation of the several types of organic matter. The plots receiving heavier additions of organic matter showed greater gains in organic substances as compared with untreated plots, than those receiving the lighter applications.

Comparisons of the effectiveness of the several organic materials for improving the content of soil organic matter should take into consideration the relative loss-on-ignition values of the substances themselves which were incorporated. These values were as follows: cultivated New Jersey peat—88 per cent, peat moss manure—89 per cent, spent mushroom soil—24 per cent, and well-rotted manure—69 per cent. After due allowance is made for differences in actual organic substance added by each type of material, it is clear that cultivated New Jersey peat was the most effective type of organic matter applied. Peat moss manure was less valuable than well-rotted manure, and the organic matter of spent mushroom soil showed the lowest increase in oxidizable material of any substance used.

The difference between spent mushroom soil and rotted manure may be explained on the basis of the rate of decomposition and the percentage of organic compounds resistant to decay, contained by the respective substances. Waksman and Nissen (4) have found that the mushroom fungus utilizes the lignin present in the manure of the mushroom beds more extensively than the cellulose and other readily decomposed constituents. On the contrary, manure undergoing decomposition in the absence of mushroom growth shows an increase in concentration of lignin and a reduction in percentage of readily decomposable constituents. Since lignin is one of the principal substances in

plant residues that resist decay, manure, being comparatively rich in this constituent, decomposes less rapidly than the organic matter of spent mushroom soil. From the standpoint of sustained improvement of the physical condition of the soil, manure therefore is more effective than the organic fraction of spent mushroom soil. For the release of nutrients for plant growth, however, manure may be expected to be less effective, since its rate of decomposition is lower.

The high persistence value of cultivated peat may also be explained on the basis of its relatively high content of lignin and other materials resistent to decay. Peat moss manure, having undergone very little decomposition has a lower content of decay-resisting compounds and therefore decomposes more rapidly than cultivated peat. From the standpoint of their persistence in the soil, the cultivated peat ranks first, well-rotted manure second, peat moss manure third, and spent mushroom soil fourth. With regard to the release of nutrients for use by plants, the order of these substances would doubtless be reversed.

SUMMARY

The improvement of the physical properties of a clay loam soil by incorporating various types of organic matter was investigated in the greenhouse with pot cultures planted to grass and supplied with an abundance of moisture. From the standpoint of the persistence in the soil of the several types of organic matter; the sustained improvement in available water-holding capacity of the soil and in its pore space, and the excellence of internal drainage resulting from the incorporation of organic substances; and the growth made by grass on treated and untreated soils, the conclusion is drawn that cultivated New Jersey peat was the most valuable substance included in the tests. Raw Michigan peat was second in value, with imported peat moss, well-rotted manure, and spent mushroom soil following in the order named.

These results were compared with a similar experiment conducted under a system of limited watering, in which the moderately fibrous materials, such as raw Michigan peat and rotted manure, proved superior. With more abundant watering, the rate of decomposition for the raw peat and manure increased, giving the advantage to the more resistant cultivated peat.

Changes occurring in the moisture holding capacities of four types of peaty materials as a result of drying were studied. The drying of each type of organic material to an air-dry condition greatly reduced the capacity for absorption, and this power was recovered very slowly with successive additions of free water. Artificial drying to a moisture content below that obtained in air-drying still further reduced the capacity for moisture absorption.

Cultivated peat was less injured by air-drying than raw peat. Imported peat moss recovered a smaller percentage of its absorptive capacity than any other type of peat, with equal opportunity for moisture absorption. The practical disadvantage in plant production arising from layers of peat below

or at the surface of the soil may be attributed to the tardy recovery of absorptive capacity following extreme drying in droughty periods. It is obvious that peats should be well mixed with the soil mass for improvement of the physical properties of the soil, and that such organic materials should not be air-dry when incorporation takes place.

Comparisons of the relative persistence of four types of organic matter in field soils over a period of two years showed that cultivated peat had raised the organic content more effectively than any other material. Well-rotted manure, peat moss manure, and spent mushroom soil followed in the order given. The rate of decomposition of the organic substance of each of the materials was correlated with the proportional content of slowly decomposable constituents such as lignin.

The respective values of these materials for improving the physical condition of soil over an extended period depend on their relative resistance to decay. The physical value of an organic substance is quite distinct from its value as a source of plant nutrients. In general, the more rapid the decomposition, the greater will be the total quantity of nutrients released. Conversely, the slower the rate of decomposition, the longer will the improvement of the soil's physical condition persist after incorporation of the organic material.

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: IX. AMPHOTERIC REACTIONS AND ISOELECTRIC WEATHERING[1]

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The various facts which have led to the present conception of the amphoteric nature of soil colloids have been presented in the preceding articles of this series of papers (16). The soil ampholytoids (amphoteric colloids) may be divided into (*a*) primary and (*b*) derived or conjugated ampholytoids.

The primary ampholytoids are represented by single compounds such as the hydroxides and oxides of aluminum and iron and by the proteins. The derived or conjugated ampholytoids represent an infinite series of complexes formed by a chemical union between (*a*) any two or more primary ampholytoids having different isoelectric points (16) and (*b*) any one ampholytoid and weak acid radicals (12).

The object now is a further study of the manner in which these materials react with simple reagents such as acids, bases, and salts and, conversely, how such reagents influence the formation, the composition, and the decomposition of the amphoteric colloidal complex. The information to be obtained by such a study would, in the first instance, enable us to characterize, by a comparatively simple test, any material of this type under investigation and would, in the second instance, enable us to account for the great variation in composition and for the conditions leading to a "degradation" (pozolization etc.) of the soil complex.

The subject will be divided into two parts of which this, the first, will be of a more general and theoretical nature, whereas the second, which immediately follows, will present the experimental work on amphoteric reactions of soil colloids.

NATURE OF COMPOUNDS

The derived or conjugated ampholytoids represent compounds of polyvalent weak acids and bases (mostly themselves insoluble) which contain residual H and OH ions by virtue of which they react as acids at high pH and as bases at low pH values. Their general formula might be written:

$$H_z \cdot A_m \cdot B_n \cdot (OH)_y$$

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

where A and B represent the anions and cations respectively and x, m, n and y the number of each ion in the colloidal micelle.

Now the amphoteric behavior of such a complex, i.e., its strength as an acid and as a base, its exchange capacity for cations and anions, its isoelectric point, its point of exchange neutrality, and its ultimate pH (the pH of the free acid-base ampholytoid after complete electrodialysis) will depend upon several factors. The amphoteric nature of the complex will, in the first place, be governed by the relative as well as by the absolute strength of the acid and basic residue. If the acid residue is strong the basic must be weak and the isoelectric point, the ultimate pH, and the point of exchange neutrality must be on the acid side. If the basic residue is the strongest then the acid residue will be correspondingly suppressed and the aforementioned points will lie on the alkaline side. These points will coincide with the neutral points only when the acid and basic residues are of the same strength (15). If both residues are very weak the amphoteric properties will be indefinite and become manifest only at high acidity and at high alkalinity.

The strength of the acid and basic residue will depend, among other things, upon the relative proportions of the reacting acid and base as well as upon their strength. It is obvious that whenever the reacting materials, such as the acid or base, as well as the products of the various steps in the reaction between them are insoluble there can be no stoichiometric relationship in the precipitate. The strength of the acid and basic residue as well as the acid and basic equivalence in the ampholytoid may therefore vary within wide limits depending upon the relative proportion and strength of the reacting acid and basic radicals. The extent to which neutralization will proceed depends, in addition to the ionization constant of water, upon the ionization constants and concentration of the several acid and basic radicals and upon the solubility products of the resulting combinations. To these must be added the dissociation of the colloid which undoubtedly exists but which cannot be defined in ordinary terms. The composition and properties of the phosphate, silicate, and ferrocyanide series, previously described (19) will serve to illustrate the foregoing.

The various steps in the mutual neutralization of weak, let us say, trivalent acids and bases of a certain type may be illustrated by a few examples. We shall assume, for illustrative purposes, the conditions to be such that neutralization proceeds to the extent that the product of the dissociation constants $k_a \cdot k_b$ of the strongest remaining acid and basic radicals has been reduced to a value of 1×10^{-17}. The neutralization may of course proceed further if the ionization of the compound formed is small enough. The ampholytoids here studied possess apparent dissociation constants of this order, as indicated by their neutralization curves. But the apparent dissociation constants of colloidal acids and bases must be magnified by the limited dissociation of their salts. The following reactions serve, however, only to illustrate the possible multitude of complexes and, in a general way, to indicate their amphoteric

behavior. The negative exponents express the value of x in the assumed dissociation constants 1×10^{-x}.

Case 1: The acid is stronger than the base but they react in equivalent quantities.

$$H^{-6}\ H^{-7}\ H^{-8}\ A + B\ OH^{-9}\ OH^{-8}\ OH^{-7} \rightarrow$$

$$H^{-8}\ A = B\ OH^{-9} + 2\,H_2O$$

In the ampholytoid the acid residue is stronger than the basic but H is equivalent to OH. The complex is isoelectric and exchange neutral on the acid side. The cation exchange capacity is moderate.

Case 2: The acid is stronger than the base and is present in excess.

$$2\,H^{-5}\ H^{-6}\ H^{-7}\ A + B\ OH^{-11}\ OH^{-9}\ OH^{-8} \rightarrow$$

$$\left.\begin{matrix} H^{-6}\ H^{-7}\ A \\ H^{-6}\ H^{-7}\ A \end{matrix}\right\rangle B\ OH^{-11} + 2\,H_2O$$

In the ampholytoid the acid residue is much stronger and is quantitatively four times as great as the basic residue. The complex is isoelectric and reacts exchange neutral at a still lower pH than the preceding one. The cation exchange capacity is very high (compare curve I, fig. 23).

Case 3: The same as case 2 except that k_a of the third H is here lower.

$$2\,H^{-5}\ H^{-6}\ H^{-10}\ A + B\ OH^{-11}\ OH^{-9}\ OH^{-8} \rightarrow$$

$$\left.\begin{matrix} H^{-6}\ H^{-10}\ A \\ H^{-6}\ H^{-10}\ A \end{matrix}\right\rangle B\ OH^{-11} + 2\,H_2O$$

In the ampholytoid the acid residue is much stronger than the basic. Of the four equivalents of H, two are as strong as in case 2 but two are considerably weaker. Since the latter two H ion are too slightly dissociated to be displaced to an appreciable extent by neutral salt cations at pH 7, the cation exchange capacity will be less than in case 2. The isoelectric point which depends upon the strongest H and OH, will, however, be the same (compare fig. 24).

Case 4: The acid is stronger than the base but the latter is in excess.

$$H^{-6}\ H^{-7}\ H^{-8}\ A + 2\,B\ OH^{-11}\ OH^{-9}\ OH^{-8} \rightarrow$$

$$H^{-8}\ A\left\langle\begin{matrix} B\ OH^{-11}\ OH^{-9} \\ \\ B\ OH^{-11}\ OH^{-9} \end{matrix}\right. + 2\,H_2O$$

In the ampholytoid the acid residue is the strongest but the basic residue is quantitatively four times as great as that of the acid. The complex is isoelectric slightly below pH 7.0 and possesses a low cation exchange capacity but

combines with great quantities of anions on the acid side of its isoelectric point (compare curve II, fig. 23).

Case 5: The acid is stronger than the base except with respect to one of the H ions. The acid is equivalent to the base.

$$H^{-3}\ H^{-7}\ H^{-9}\ A + B\ OH^{-6}\ OH^{-8}\ OH^{-7} \rightarrow$$

$$H^{-9}\ A = B\ OH^{-6} + 2\,H_2O$$

In the ampholytoid the basic residue is stronger than the acid residue. The complex is isoelectric and reacts exchange neutral on the alkaline side. The cation exchange capacity is very small if any. (Because of the low dissociation of the exchangeable cations, especially the divalent ones, the H ions may be displaced at a lower pH than that calculated by the buffer equation upon which the curves are based.

Case 6: The acid and base are of equal strength but two of the dissociation constants are very low.

$$H^{-7}\ H^{-10}\ H^{-13}\ A + B\ OH^{-12}\ OH^{-10}\ OH^{-7} \rightarrow$$

$$H^{-10}\ H^{-12}\ A \cdot B\ OH^{-13}\ OH^{-10} + H_2O$$

There results then an ampholytoid in which the acid and basic residues are both very weak. The product, $k_a \cdot k_b = 1 \times 10^{-20}$, is low and the amphoteric properties are suppressed over a considerable pH range. The complex ought to be isoelectric throughout this range but will, like all inert substances, be electronegative down to a low pH at which the complex combines with a sufficient number of diffusible anions whose dissociation will create a positive charge large enough to balance this "residual" negative charge. (Since even air bubbles are known to carry a negative charge we must ascribe this charge to the water itself; either to an orientation of its molecules or to an unequal distribution of its ions, H and OH, at the interface).

The aforementioned six cases are sufficient to indicate the practically infinite number of combinations. It is obvious that in a colloidal aggregate containing thousands or even millions (11) of molecules almost any relationship as to the strength and quantity of the acid and basic residue is possible. Among the complexes which thus far have been prepared and studied examples will be found which will fit most of the preceding assumed combinations (12).

NEUTRALIZATION

In order to obtain an idea of the general form of the neutralization curves to be expected from such combinations and for a comparison with the experimental curves of the various complexes to be shown later (part X) we shall now plot theoretical neutralization curves of the preceding hypothetical combinations. But to be able to do this at all we shall be compelled to use an equation which expresses only in a general way the much more complicated actual relationship. We shall make use of the buffer equation which applies

to the neutralization of a weak acid by a strong base or vice versa. If the salt of a weak acid is completely dissociated the mass law implies the equation (5).

$$[H^+] = k.\frac{\text{concentration of free acid}}{\text{concentration of salt}}$$

where k is the dissociation constant of the acid. This equation is only a near approximation unless account is taken of the activity coefficient of the anions of the salt (17). Now, if c represents the total concentration of free acid plus combined acid, i.e., acid anions, and x the concentration of the salt, i.e., acid anions, then

$$[H^+] = k.\frac{c - x}{x}$$

or

$$x = \frac{c}{1 + \frac{[H^+]}{k}}$$

Henderson (6) believes the law to apply to the neutralization of complex substances like the proteins which contain several acid and basic radicals. If we now likewise assume the equation to apply to our hypothetical complex containing several acid radicals of apparent dissociation constants k_1, k_2, k_3 ... and if x_1, x_2, x_3 ... represent the concentration of base in combination with them, then the relationships become

$$x_1 = \frac{c}{1 + \frac{[H^+]}{k_1}}$$

$$x_2 = \frac{c}{1 + \frac{[H^+]}{k_2}}$$

$$x_3 = \frac{c}{1 + \frac{[H^+]}{k_3}} \text{ etc.}$$

The total concentration of base in combination with all the acid groups will be the sum of all the x's

$$\Sigma x = x_1 + x_2 + x_3 + \cdots$$

The corresponding expressions for the neutralization of weak basic radicals by a strong acid become

$$y_1 = \frac{c}{1 + \frac{[OH^-]}{k'_1}}$$

$$y_2 = \frac{c}{1 + \frac{[OH^-]}{k'_2}}$$

$$y_3 = \frac{c}{1 + \frac{[OH^-]}{k'_3}} \text{ etc.}$$

and

$$\Sigma y = y_1 + y_2 + y_3 + \cdots$$

where y_1, y_2, y_3, ... represent the acid in combination with the basic radicals and k'_1, k_2', k'_3, ... their dissociation constants.

In the combination in the foregoing case 2, the acid dissociation constants $k_1 = k_2 = 1 \times 10^{-6}$, $k_3 = k_4 = 1 \times 10^{-7}$, and the base constant $k' = 1 \times 10^{-11}$ were assumed. Putting $c = 1$, the computation of the quantities of base

TABLE 90

Theoretical capacity to neutralize base when $k_1 = k_2 = 1 \times 10^{-6}$, $k_3 = k_4 = 1 \times 10^{-7}$

$[H^+]N$..... / $[OH^-]N$...	10^{-0} / 10^{-14}	10^{-1} / 10^{-13}	10^{-2} / 10^{-12}	10^{-3} / 10^{-11}	10^{-4} / 10^{-10}	10^{-5} / 10^{-9}	10^{-6} / 10^{-8}	10^{-7} / 10^{-7}	10^{-8} / 10^{-6}	10^{-9} / 10^{-5}	10^{-10} / 10^{-4}	11^{-11} / 10^{-3}	10^{-12} / 10^{-2}	10^{-13} / 10^{-1}
x_1	.....	.....	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00	1.00	1.00	1.00	1.00
x_2	.....	.....	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00	1.00	1.00	1.00	1.00
x_3	.....	.....	.....	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00	1.00	1.00	1.00
x_4	.....	.....	.....	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00	1.00	1.00	1.00
Σx	0	0	0	0	0.02	0.20	1.18	2.82	3.80	3.98	4.00	4.00	4.00	4.00

Capacity to neutralize acid when $k' = 1 \times 10^{-11}$

y	1.00	0.99	0.91	0.50	0.09	0.01	.....	.....	.....	.....	.....	.....	.....	.....
$\Sigma x - y$	−1.00	−0.99	−0.91	−0.50	−0.07	0.19	1.18	2.82	3.80	3.98	4.00	4.00	4.00	4.00
$\Sigma x + y$	1.00	0.99	0.91	0.50	0.11	0.21	1.18	2.82	3.80	3.98	4.00	4.00	4.00	4.00

(x) in combination with the acid radicals and of the quantities of acid (y) in combination with the basic radical at various $[H^+]$ yields approximately the values in table 90.

The figures show that $\Sigma x + y$, that is, the amount of acid in combination with the acid radical plus the amount of base in combination with the acid radicals of the ampholyte, is at a minimum somewhere between pH 4 and 5. At this point $\Sigma x - y = 0$ and this should be the isoelectric point, at least if the two salts of the ampholyte are equally dissociated.[2]

[2] But in his mathematical analysis of the problem Michaelis (17) comes to the "very remarkable conclusion" that even if true salt formation takes place on one side or the other, that is, even if the combination with the acid should be less dissociated than the combination with the base or vice versa, the isoelectric point must remain the same. This conclusion

It is clear that if the dissociation constant of the strongest acid radical of the compound in table 90 were increased to 1×10^{-5}, the minimum in the values $\Sigma x + y$ and $\Sigma x - y$ would occur at a lower pH, that is to say, the compound would have a lower isoelectric point. A strengthening of the basic radical would have the opposite effect. The formula

$$I = \sqrt{\frac{k_a}{k_b}\, k_w},$$

where I represents the isoelectric $[H^+]$ and k_w the dissociation constant of water, is another expression for this relation. The isoelectric point of an ampholyte for which $k_a = 1 \times 10^{-6}$ and $k_b = 1 \times 10^{-11}$ is then

$$I = \sqrt{\frac{10^{-6}}{10^{-11}} \cdot 10^{-14}} = \sqrt{10^{-9}} = \text{pH } 4.5$$

The compound in table 90 contains two acid radicals for which $k_a = 1 \times 10^{-6}$. The isoelectric point of this ampholyte lies therefore somewhat below pH 4.5. This is illustrated by curve I in figure 23, in which the $\Sigma x - y$ values, which represent the net amount of base (positive values) and of acid (negative values) in combination, are plotted against $[H^+]$. The dotted lines represent the separate curves of Σx and Σy.

Curve II, figure 23, represents the theoretical neutralization of the combination in the aforementioned case 4. In this compound the basic residue is four times as great as the acid, but the latter radical is stronger than the strongest basic radical. The compound is therefore isoelectric on the acid side, but this point lies in this case only slightly below pH 7.

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becomes perhaps comprehensible if we consider that the charge on the ampholyte ions is not alone governed by the dissociation of its salt but also by the dissociation of the remaining undisplaced OH and H. The latter must remain the same at the same pH. Therefore, if an acid or base be added to an ampholyte with which a slightly dissociated compound is formed the only result will be that more of the acid or base will combine at the given pH. The ultimate state of ionization will be the same. In other words the degree of charge (17), which at the isoelectric point equals zero, will be the same, but the point of exchange neutrality, that is, the point at which the ampholyte combines with an equal number of anions and cations will be deflected.

It remains to explain the fact established in a previous article of this series (12) that the more strongly the different anions are adsorbed by the ampholytoid, that is, the less these ions are dissociated by the complex, the greater is the displacement of the isoelectric point to the acid side. Thus the sulfated complex is isoelectric at a lower pH than the chloridated complex, and the phosphated complex is isoelectric at a still lower pH.

The explanation of this influence is that the entrance of these ions in the complex changes its amphoteric nature. Some of the phosphate valences have combined with an equal number of the basic radicals while the remainder of the phosphate valences have added to the strength and number of the acid radicals of the complex whose acid residue has thus been increased while its basic residue has been decreased. In other words, a new complex has been formed in which k_a is larger and k_b is smaller. This was shown by an increase in the cation exchange capacity (15).

Figure 24 gives the neutralization curve of the compound assumed in case 3, in which two of the four acid radicals are very weak. This compound will neutralize as much base as the one represented by curve I, figure 23, which has the same isoelectric point, but only at higher alkalinity. Similar neutralization curves are obtained from soil colloids having a high sesquioxide content. Their cation exchange capacity at pH 7 may be very low but at high pH these

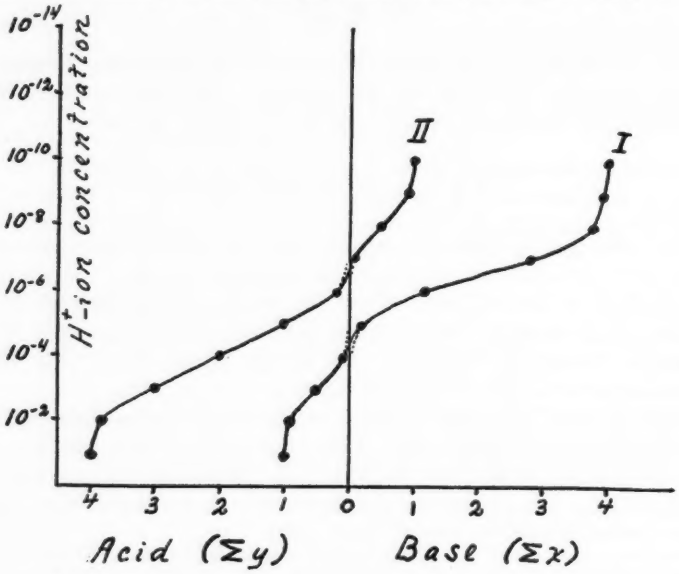

FIG. 23. THEORETICAL NEUTRALIZATION CURVES OF AN AMPHOLYTE

I, of the type

$$\begin{matrix} H^{-6}H^{-7}A \diagdown \\ \qquad\quad B\,OH^{-11} \\ H^{-6}H^{-7}A \diagup \end{matrix}$$

II, of the type

$$\begin{matrix} \qquad\quad \diagup B\,OH^{-11}\,OH^{-9} \\ H^{-8}A \\ \qquad\quad \diagdown B\,OH^{-11}\,OH^{-9} \end{matrix}$$

(Negative exponents = x in the dissociation constants 1×10^{-x}. A and B represent acid and basic radicals respectively.)

colloids adsorb large quantities of bases, as a result of the sesquioxides (10). The amphoteric $Al(OH)_3$ and $Fe(OH)_3$ are stronger as bases than as acids and have therefore relatively low k_a values.

The unbroken lines in figure 25 show the theoretical neutralization curve of an ampholyte in which both the acid and basic residues are very weak. The curve represents the compound assumed in the aforementioned case 6. Some proteins as well as certain inorganic ampholytoids yield curves of this type.

EFFECTS OF LIMITED DISSOCIATION OF COLLOIDAL SALTS

Salts of colloidal ampholytes dissociate apparently to a very limited extent even when the combination is potentially soluble. Thus sodium phosphate, for example, is soluble but the sodium aluminum phosphate complex is only colloidally dispersible. Each micelle may consist of hundreds of thousands or even millions of molecules. If now all of the Na ions were dissociated by the complex, a potential difference far greater than the assumed critical value of 70 millivolts would be attained (12). We have assumed this to be the cause of

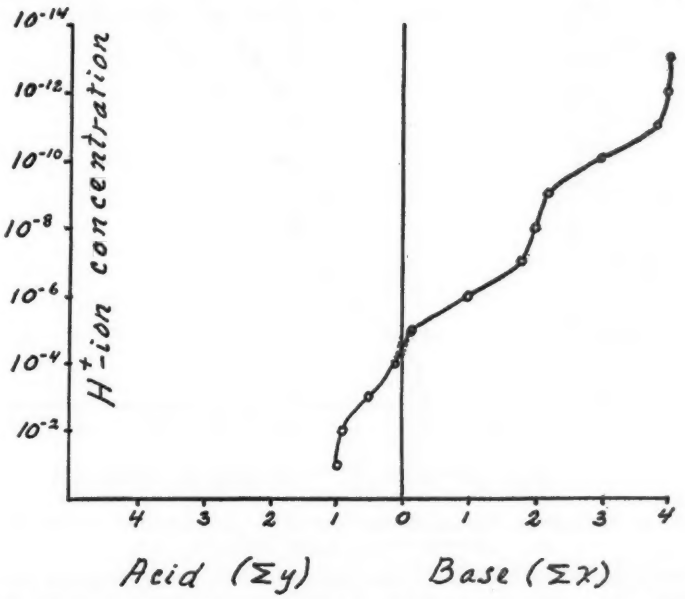

FIG. 24. THEORETICAL NEUTRALIZATION CURVES OF AN AMPHOLYTE OF THE TYPE

$$\begin{matrix} H^{-6}H^{-10}A \\ \\ H^{-6}H^{-10}A \end{matrix} \diagdown\!\diagup B\,OH^{-11}$$

the limited dissociation of colloidal salts, which is quite evident, among other things, from the fact that the H^+ ions are displaceable by neutral salt cations.

The effect of this limited dissociation of colloidal salts will be such that the acid and the basic radicals of the colloid will appear stronger the less dissociated the compounds formed with the diffusible cations and anions respectively. Thus a given soil adsorbs more $Ca(OH)_2$ than NaOH at a given pH and the "unsaturated" soil develops a greater exchange acidity with $CaCl_2$ than with NaCl (14). The neutralization curves in figure 23 to 25, which are based

on the assumption of complete dissociation of the salts, will, under such conditions, have a different form. The curves will be deflected in the direction of the broken lines as indicated in figure 25. The apparent dissociation constant of the acid and the basic radicals will be greater.

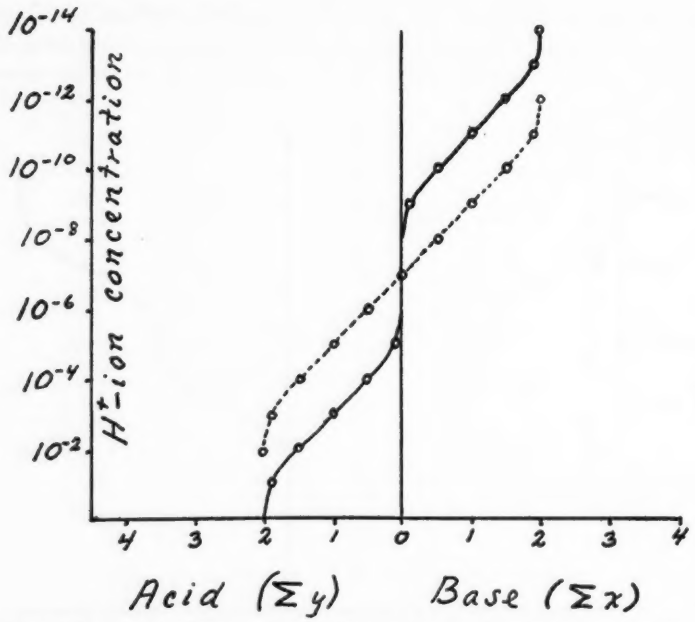

FIG. 25. THEORETICAL NEUTRALIZATION CURVES OF AN AMPHOLYTE OF THE TYPE $H^{-10}\,H^{-12}\,A - B\,OH^{-12}\,OH^{-10}$

Broken lines indicate deflection of the curves when incompletely dissociated salts are formed.

HYDROLYSIS

Our scheme of presentation has thus far been based on the assumption that it is only the acid and basic residues of the compounds between weak acids and bases which combine to form salts with strong bases and acids respectively. The compound formed by the partial union of the weak acid and base was considered a stable one. But, except at pH values near the isoelectric point the reaction does not stop here. In solutions of high alkalinity or acidity compounds of this nature undergo more or less extensive hydrolysis. This can be observed by the change in color of certain colored complexes such as ferric "phosphate" and "ferrocyanide" upon the addition of a little alkali.

The hydrolysis of proteins into amino acids is of a similar type. Thus the reaction involving a simple neutralization of the acid residue by a strong base

$$\begin{array}{l} H\,A = B\,OH + Na\,OH \rightarrow \\ Na\,A = B\,OH + H_2O \end{array}$$

becomes hydrolytic in the presence of an excess of base, thus

$$\begin{array}{l} Na\,A = B\,OH + Na\,OH \rightarrow \\ Na_2\,A - B(OH)_2 \end{array}$$

This hydrolysis results finally in a complete decomposition as follows

$$\begin{array}{l} Na_2\,A - B(OH)_2 + Na\,OH \rightarrow \\ Na_3\,A + B(OH)_3 \end{array}$$

TABLE 91

Theoretical capacity to neutralize base when $k_1 = 1 \times 10^{-5}$, $k_2 = 1 \times 10^{-6}$, $k_3 = 1 \times 10^{-7}$

$[H^+]$ ..... $[OH^-]$	10^{-1} 10^{-13}	10^{-2} 10^{-12}	10^{-3} 10^{-11}	10^{-4} 10^{-10}	10^{-5} 10^{-9}	10^{-6} 10^{-8}	10^{-7} 10^{-7}	10^{-8} 10^{-6}	10^{-9} 10^{-5}	10^{-10} 10^{-4}
x_1	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00	1.00	1.00
x_2	.....	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00	1.00
x_3	.....	.....	.....	.....	0.01	0.09	0.50	0.91	0.99	1.00
Σx	.....	.....	0.01	0.10	0.60	1.50	2.40	2.90	2.99	3.00
Capacity to neutralize acid when $k'_1 = 1 \times 10^{-3}$, $k'_2 = 1 \times 10^{-9}$, $k'_3 = 1 \times 10^{-10}$										
y_1	1.00	1.00	1.00	0.99	0.91	0.50	0.09	0.01	....	....
y_2	1.00	1.00	0.99	0.91	0.50	0.09	0.01	....	....	....
y_3	1.00	0.99	0.91	0.50	0.09	0.01	....	....	....	....
Σy	3.00	2.99	2.90	2.40	1.50	0.60	0.10	0.01	....	....
$\Sigma x - y$	−3.00	−2.99	−2.89	−2.30	−0.90	0.90	2.30	2.89	2.99	3.00
$\Sigma x + y$	3.00	2.99	2.91	2.50	2.10	2.10	2.50	2.91	2.99	3.00

In the presence of an excess of a strong acid the ultimate result would be

$$\begin{array}{l} H\,A = B\,OH + 3\,H\,Cl \rightarrow \\ B\,Cl_3 + H_3A + H_2O \end{array}$$

The extent to which these reactions proceed depends of course upon the "stability," i.e., the dissociation of the compound.

These reactions play an important rôle in the soil. It is because of this hydrolysis that the cation exchange capacity can be "built up" (14), and the two extreme types of soil transformation, namely podzolization and laterization, represent in all probability nothing but an acid hydrolysis in the first case and a basic hydrolysis in the second case. The following illustration will serve here to show the significance of such hydrolytic reactions.

Assume a mixture of a weak acid and base. Let the dissociation constants of the acid radicals be $k_1 = 1 \times 10^{-5}$, $k_2 = 1 \times 10^{-6}$, $k_3 = 1 \times 10^{-7}$ and of the basic radicals, $k'_1 = 1 \times 10^{-8}$, $k'_2 = 1 \times 10^{-9}$, and $k'_3 = 1 \times 10^{-10}$. If we again assume the buffer equation to apply, we obtain the capacities to combine with bases and acids as given in table 91.

If the conditions to which the buffer equation applies, i.e., complete solubility and dissociation of the salt, prevailed, then the neutralization of the acid and the basic radicals would overlap in the $[H^+]$ range between 10^{-3} and 10^{-8}. This means that the weak acid and base would partly neutralize each other within this range. This salt formation between the two components would attain a maximum in this particular case, at pH 5.5 where $\Sigma x - y = 0$.

The ionic equilibria are best seen in figure 26, where the ordinates represent the degree of salt formation, i.e., Σx of the acid radicals (A) and Σy, of the basic radicals (B). The following points are significant:

At B^{+++} the basic radicals are almost completely neutralized.
At A^{---} the acid radicals are almost completely neutralized.
At H_3A the acid radicals are almost wholly undissociated.
At $B(OH)_3$ the basic radicals are almost wholly undissociated.
At I there is a maximum combination between A and B.

The acid and basic residue at I is represented by the distances I A^{---} and I B^{+++} respectively, which on the ordinate axis correspond to nearly two of the three radicals. The compound is therefore here approximately

$$H_3 A - B(OH)_3$$

The addition of a strong acid will lead to a salt formation with the basic radicals, which will be almost completely neutralized at $[H^+] = 10^{-2}$, whereas the acid radicals pass into the practically undissociated condition at $[H^+] = 10^{-3}$. Above this hydrogen-ion concentration there can be no union between A and B. The acid hydrolysis will here be complete. The addition of a strong base will have the opposite effect. The acid radicals will be almost completely neutralized at $[H^+] = 10^{-9}$ and the basic radicals will be practically undissociated at $[H^+] = 10^{-8}$. Below this hydrogen-ion concentration there can again be no compound formation between A and B. The basic hydrolysis will here be complete.

Below a pH of 5.5 the cation B^{+++} of the basic radicals predominates in the solution whereas at higher pH the anion A^{---} of the acid radicals is in excess. Now it is obvious that if the compound, let us say $H_3A \cdot B(OH)_3$, did not ionize to any appreciable extent or if it were insoluble, that is, existed in the form of a colloidal complex, then the point I would be the isoelectric point. At pH below 5.5 the compound would react with acids, e.g., HCl, and assume a positive charge thus

$$H_3A \cdot B(OH)_3 + H\,Cl \rightarrow$$
$$H_3A \cdot B^+OH + Cl^- + H_2O$$

At higher pH the reaction with bases, e.g., NaOH would yield an anion thus

$$H_2A \cdot B(OH)_2 + Na\ OH \rightarrow$$
$$H\ A^- \cdot B(OH)_2 + Na^+ + H_2O$$

APPLICATION TO INSOLUBLE COMPOUNDS

The formation of an insoluble compound would, however, greatly affect the ionic equilibrium of the system. The foregoing simple relationship has been used solely for the purpose of illustrating reactions which may be quantitatively very different but which are at least of the same nature. The difficulty is that the reactions of colloidal iongens cannot be expressed in terms of the

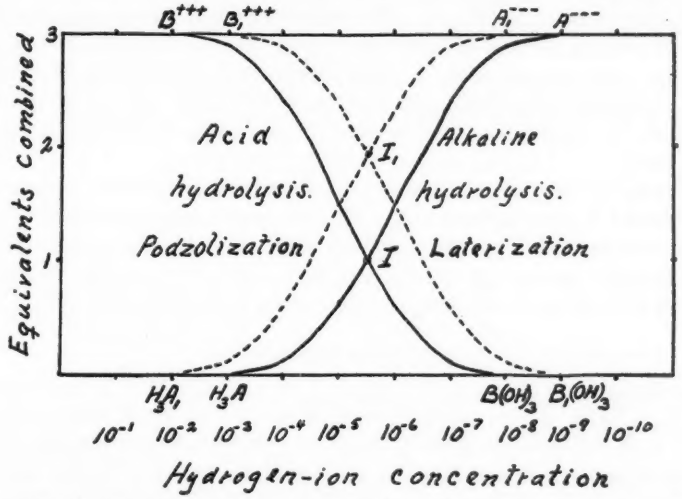

FIG. 26. THEORETICAL NEUTRALIZATION OF A TRI-BASIC ACID WHOSE DISSOCIATION CONSTANTS ARE $k_1 = 1 \times 10^{-5}$, $k_2 = 1 \times 10^{-6}$, AND $k_3 = 1 \times 10^{-7}$, AND OF A TRI-ACIDIC BASE WHOSE CONSTANTS ARE $k'_1 = 1 \times 10^{-8}$, $k'_2 = 1 \times 10^{-9}$, AND $k'_3 = 1 \times 10^{-10}$

The broken lines indicate deflection of the curves when the acid and the base form a slightly dissociated and insoluble compound. There results then an amphoteric colloid of the type H A = B OH and isoelectric at I_1.

mass law. Michaelis (17) has analyzed some of the complications arising in the aforementioned dissociation law in cases where undissociated salts are formed with mono- and divalent ions and also in cases of micelle formation, i.e., aggregation of two or more molecules (18). But it would be extremely difficult if at all possible to find a quantitative expression for a reaction so complex as that, let us say, between aluminum hydroxide and silicic or even phosphoric acid.

It is, however, obvious that if a slightly soluble salt is formed the degree of salt formation will be greater the lower the ionic product of the salt and that,

because of the removal of the ions of the salt, the residual acid and basic radicals will be stronger. This is illustrated in figure 26 by the dotted lines which show the direction of the displacement of the neutralization curves under such conditions. The extent of this displacement depends of course upon the ionic product of the compound. The position of I_1 remains, in this particular case, where the acid and base are present in equivalent quantities and where the acid and basic residues maintain the same relative strength, the same as that of I.

The significant thing is also the magnitude of the acid and basic residues which have become much smaller. It is obvious that if the compound between A, and B, were completely undissociated a normal salt with no acid or basic residue would be formed. This compound would then not react amphoterically except perhaps by hydrolytic cleavage at very low and very high pH values. Also, the greater the acid and basic residues, that is to say, the greater the ion product of the compound, the greater will be the strength of the free radicals, but the compound will be more subject to hydrolysis and therefore less stable.

Among the inorganic compounds studied we have encountered types which correspond to both extremes (13). Thus the ionic exchange reactions of certain "sulfides" (e.g. Sb and Bi) indicate a weak acid residue and great stability, whereas the "sulfide" of tin and especially ferric "ferrocyanide" possess a strong acid residue but are quite unstable even at a pH as low as 7.0 (19).

MAXIMUM STABILITY

It is clear that the insoluble compound, let us designate it by the formula $H\,A_1 = B_1OH$, is both chemically and physically most stable at the point I_1, that is, at the isoelectric point or at pH 5.5. There is here a maximum combination between A_1 and B_1. The number of anions $^-A_1 = B_1OH$ and the number of cations $H\,A_1 = B_1^+$ are equal and their sum is here at a minimum. The absence of an electric charge gives rise to an extensive aggregation. The material will become coarse-grained and difficult to disperse. If a solution of, let us say, NaCl of pH 5.5, is added to a suspension of the compound there will be no appreciable change in pH. As a result of the limited dissociation of all salts of colloids there may be some displacement of the OH and H ions by the anions and cations of the salt even at the isoelectric point but this double displacement will be equivalent and the colloid will react "exchange-neutral." [This is only true if the compound formed with the anions and cations of the salt are equally ionized. With NaCl this has been found to be approximately true for many colloids because at the isoelectric point approximately equal quantities of Na and Cl ions were found to be adsorbed. The SO_4 ions, it may be recalled (15), were adsorbed in considerable excess of the Na ions at the isoelectric point. When such differences in "adsorbability" occur it is obvious that the point of exchange neutrality does not coincide with the isoelectric point].

At the isoelectric point the compound will be least reactive, least hydrolytically decomposed, least soluble, and least dispersible.

ULTIMATE pH

The reaction of a suspension of the free compound $H\,A_1 = B_1OH$ will be acid since the acid radical is stronger than the basic. Its pH will lie between the neutral and the isoelectric points and will, in concentrated suspensions, approach but never quite attain the latter point. In the free state the compound must be electronegative since more H^+ than OH^- ions are dissociated. A trace of free acid must be added to increase the ionization of the basic radicals and suppress that of the acid radicals before the compound can be isoelectric. The pH of a concentrated suspension of the free ampholyte is, like the isoelectric point, determined by the relative strength of the acid and basic radicals. To this pH we apply the term "ultimate pH."

Let us illustrate the relationship between the ultimate pH and the isoelectric pH as follows: In a system containing the free compound $H\,A_1 = B_1OH$

$$[H^+] + [A_1^- = B_1\,OH] > [H\,A_1 = B_1^+] + [OH^-]$$

or

$$[H^+] > [OH^-]$$

since the acid radical is, in the case considered, stronger than the basic radical.

At the isoelectric point we have by definition

$$[A_1^- = B_1\,OH] = [H\,A_1 = B_1^+]$$

To render the free compound isoelectric we must increase the dissociation of the basic radical by the addition of an acid S which combines with the compound to form $H\,A_1 = B^+ + S^-$.

The system will be isoelectric when

$$[H^+] + [A_1^- = B_1\,OH] = [H\,A_1 = B_1^+] + [S^-] + [OH^-]$$

or when

$$[S^-] = [H^+] - [OH^-]$$

The amount of acid required will depend largely upon the dissociation of the compound which the acid forms with the colloid. The quantitative relationship is therefore different from that of the much simpler systems of soluble ampholytes [comp. Sörensen (21) and Michaelis (17)].

EXCHANGE ACIDITY AND ALKALINITY

If an acidified solution of NaCl having a pH below that of the isoelectric point is added to the suspension of the free amphoteric colloid it will be found that the pH is increased, that is, acid has been neutralized. The material yields an "exchange alkalinity" on the acid side of the isoelectric point. This

is because the basic radical is here alone reactive and combines with the anion of the salt. If the NaCl solution is less acid than the acidity corresponding to the isoelectric point, an "exchange acidity" will be developed. In this case the acid radicals combine with the cation of the salt. The reactions may be formulated as follows:

$$H\ A_1 = B_1\ OH + Na\ Cl \rightleftarrows H\ A_1 = B_1\ Cl + Na\ OH$$

at pH below the isoelectric point and

$$H\ A_1 = B_1\ OH + Na\ Cl \rightleftarrows Na\ A_1 = B_1\ OH + HCl$$

at pH above the isoelectric point.

In the case of soluble and completely ionized salts of ampholytes this neutral salt decomposition could not take place. The explanation of the fact that the reactions are brought about by colloids is that all colloidal salts, as well as the acids and bases, ionize to a limited extent.

The preceding reactions are very useful in the study of the amphoteric soil colloids. Their application will be discussed in the experimental part of this work.

ACID AND BASIC HYDROLYSIS

Let us now consider the general behavior of the compound on the acid and alkaline sides of the isoelectric point.

On the acid side the compound will react with the stronger acid responsible for the lowering of the pH. The ionization of the basic radicals will increase whereas that of the acid radicals will be suppressed. The ion $H\ A_1 = B_1^+$ will predominate and the complex will carry a positive charge and be more dispersible. But at the same time there will be some hydrolytic cleavage of the compound, which ionizes also to a slight extent into $H\ A_1^- - B_1^+\ OH$ and $HA_1^{--} + B_1^{++}\ OH$. There will therefore be formed, first, the ionic species $HA_1 = B^+$ and $H_2A_1 - B_1^{++}$ and then, at a still lower pH, the ions B_1^{+++} and the undissociated molecules of the acid H_3A_1. We shall, therefore, have all degrees of dispersibility down to single ions.

The ionic equilibrium at any one pH will greatly depend upon the nature of the acid with which the compound reacts. Thus it makes a great difference in respect to the dispersibility whether the acid anions are mono-, di-, or trivalent and whether or not they form soluble or slightly soluble compounds with the base $B_1\ (OH)_3$. Only monovalent anions would result in a strong positive charge and a maximum dispersion of the complex (11). If the acid is tribasic and therefore also a weak acid and if it forms a slightly soluble compound with the base then there will at first be formed a new complex in which the acid residue is stronger and the basic residue is weaker. This complex will therefore be isoelectric at a lower pH and possess a greater cation exchange capacity, as has been experimentally verified by the phosphated soil complex (15).

Let us illustrate this by the following reaction

$$H_3A + H_2A_1 - B_1OH_3 \rightarrow$$

$$\begin{matrix} H_2A_1 \\ \\ H_2A \end{matrix} \Big\rangle B_1OH + H_2O$$

The result is the same if the original compound had been formed with an excess of the weak acid. But even this complex will undergo a hydrolytic cleavage and disintegrate at still a lower pH, thus

$$\begin{matrix} H_2A_1 \\ \\ H_2A \end{matrix} \Big\rangle B_1OH + 3HCl \rightarrow$$

$$B_1Cl_3 + H_3A + H_3A_1 + H_2O$$

On the alkaline side of the isoelectric point the compound will react with the stronger base responsible for the increase in pH. The ionization of the acid radical will increase, whereas that of the basic radical will be suppressed. The ion $A_1^- = B\ OH$ will predominate and the complex will carry a negative charge. But here again there will be some hydrolytic cleavage of the compound resulting in the ionic species $A_1^- = B_1OH$, $A_1^{--} - B(OH)_2$, A_1^{---} and in undissociated molecules of the base $B_1(OH)_3$.

The ionic equilibrium, the dispersibility, and the solubility at any one pH will be greatly modified by the nature of the base with which the acid radicals react. The alkali hydroxides will impart a strong negative charge, a high dispersion, and, at high pH, a considerable solution. The alkaline earth bases, which form slightly dissociated and slightly soluble combinations with the acid radicals, will impart a weak negative charge, a small tendency to disperse, and only a slight degree of solution. The divalent cations will therefore retard the disintegration and the readjustment in the composition of the complex in its otherwise unstable electronegative condition.

The weak trivalent bases, which form highly insoluble and very slightly dissociated compounds with the acid radicals, will form a new amphoteric complex in which the acid residue is repressed while the basic residue is augmented. The complex will be isoelectric at a higher pH and will have a lower cation exchange capacity. (The trivalent cations in the soil are displaceable by hydrolytic cleavage but not by the neutral salt cations.) The reaction between a trivalent base and the amphoteric compound may be illustrated by the equation:

$$B(OH)_3 + H_2A_1 - B_1(OH)_2 \rightarrow$$

$$HA_1 \begin{matrix} \diagup B_1(OH)_2 \\ \\ \diagdown B\ (OH)_2 \end{matrix} + H_2O$$

At high pH, that is to say, in the presence of free alkali, this complex, like the original one, undergoes hydrolysis as follows

$$\mathrm{H\,A_1}\begin{matrix}\diagup \mathrm{B_1\,(OH)_2} \\ \diagdown \mathrm{B\,(OH)_2}\end{matrix} + 2\,\mathrm{Na\,OH} \rightarrow$$

$$\mathrm{Na_2A_1 - B_1(OH)_2 + B(OH)_3 + H_2O}$$

and

$$\mathrm{Na_2A_1 - B_1(OH)_2 + Na\,OH} \rightarrow$$

$$\mathrm{Na_3A_1 + B_1(OH)_3}$$

An experimental proof of these reactions was presented in a previous chapter where it was shown that the "aluminated" soil complex is isoelectric at a high pH and possesses a lower cation exchange capacity. The fact that the latter could be partly restored by treating the colloid with alkali points to a hydrolytic cleavage according to the foregoing equations (14).

ISOELECTRIC WEATHERING

If we now should attempt to apply these theories to the conditions prevailing in soils, we must first take account of the fact that in the soil, soluble and even colloidally dispersed materials follow the movement of the water. This means a more or less continuous removal of the soluble or highly dispersible products of a reaction from the insoluble and less dispersible products. It is in general true that materials in the ionized condition are more soluble than in the molecular condition just as colloids are more dispersible in the charged than in the isoelectric condition. It is also true that an amphoteric colloid is least ionized at the isoelectric point.

These facts taken together lead us to the significant conclusion that amphoteric colloids of the type here considered possess a tendency to alter their composition in such a way that their isoelectric point coincides with the prevailing pH. Let us illustrate this statement by two examples.

Assume the compound represented in figure 26 (dotted lines) to be subjected to a continuous leaching with a solution at pH 4.5. The basic radicals would be highly ionized at this pH and would, by hydrolytic cleavage, be freed from the insoluble complex and removed by the solution. At pH 4.5 the acid radicals would still possess some combining power and would bind some of the basic radicals. The basic residue would, however, be small whereas the acid residue would be large. Instead of the compound $\mathrm{H\,A_1 = B_1OH}$ the complex would more nearly correspond to

$$\begin{matrix}\mathrm{H_2\,A_1}\diagdown \\ \qquad\quad \mathrm{B_1\,OH} \\ \mathrm{H_2\,A_1}\diagup\end{matrix}$$

which, let us say, is isoelectric at pH 4.5. At this point the remaining basic radical would be no more reactive than the acid radicals. They would once more be equally ionized and the complex would be stable, beyond its solubility.

The ultimate result of a prolonged leaching with a solution of a constant pH would, within certain limits, be a complex of such composition as to be isoelectric at the prevailing pH of the leaching solution. The preceding process represents an acid hydrolysis and is represented in nature by the process of podzolization.

Assume now the same original compound to be subjected to a continuous leaching with a solution at pH 6.5. The acid radicals would now be the ones to be highly ionized and would, by hydrolytic cleavage, be freed from the complex and removed by the solution. Here again a stable complex would ultimately be formed at the point where a certain amount of the acid radicals had been lost and where the acid and basic residues once more possessed the same reactivity. The new complex, isoelectric at 6.5, would contain a small acid residue whereas the basic residue would be large. From figure 26 we may assume the composition of the ultimate product of this basic hydrolysis to be approximately

$$H A_1 \begin{cases} B_1 (OH)_2 \\ B_1 (OH)_2 \end{cases}$$

It is clear that if the leaching solution had a still higher pH, let us say 7.5, the ultimate composition of the complex, isoelectric at this pH, would represent a still smaller acid content and a still larger basic content. This basic hydrolysis is represented in nature by the process of laterization.

CLIMATE, pH AND COMPOSITION

To summarize let us state our conclusions as follows:

The tendencies in the process of weathering will always be toward the formation of compounds possessing a maximum stability both physically and chemically. This maximum stability, or minimum reactivity, is represented by the isoelectric condition of the ampholytoids. Since now the isoelectric composition of this type of material varies with the pH we should expect a relationship to exist between the composition of the soil colloidal complex and the prevailing hydrogen-ion concentration of the soil solution.

This relationship can, of course, only be fully expressed under conditions of sufficient rainfall to cause extensive leaching and then only in a very general way, because of local differences in climate, geology, etc. Another prerequisite for such a relationship to become manifest is that the climatic conditions must have remained approximately the same for a long period. We shall now look for what evidence we may find.

Let us first briefly review the laws of isoelectric precipitation as experimentally established for the materials in question. Figure 27, which relates

the composition to the isoelectric pH of the aluminum and iron silicate systems, will serve to indicate in a general way what we might expect to happen under natural conditions. The figure is adapted from one in an earlier publication (13).

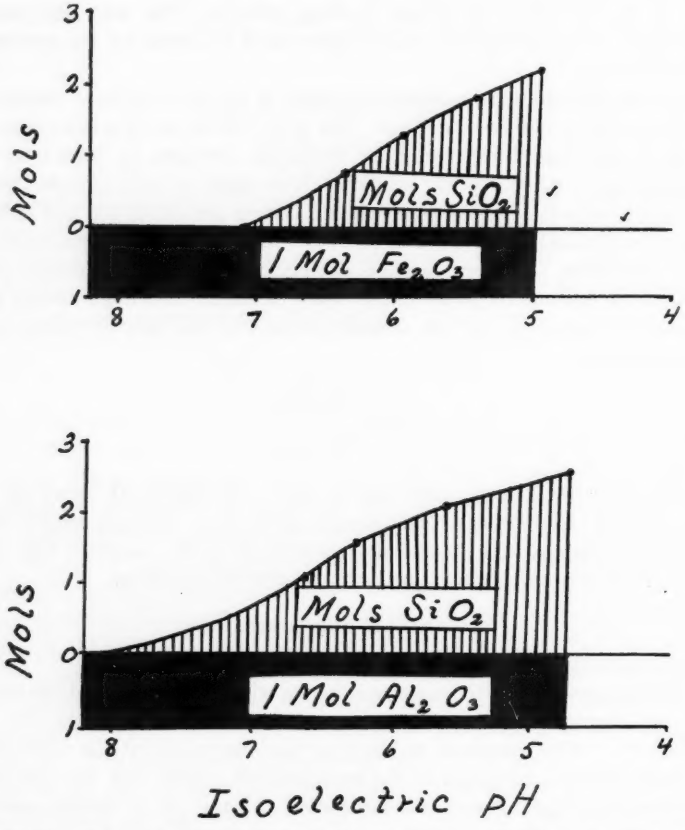

FIG. 27. THE NUMBER OF MOLS OF SILICA ISOELECTRICALLY PRECIPITATED BY 1 MOL ALUMINUM AND FERRIC OXIDE AT VARIOUS pH

COMPARATIVE BEHAVIOR OF ALUMINUM AND IRON

It will be noted that the proportion of silicic acid isoelectrically precipitated by aluminum and iron increases as the pH decreases and that aluminum hydroxide, being a stronger base than ferric hydroxide, binds the greatest proportion of the acid at any given pH. Aluminum and ferric "hydroxides" when precipitated from the chlorides are isoelectric at about pH 8.1 and 7.1 respect-

ively. Aluminum "silicate" can therefore begin to form at a higher pH than ferric "silicate."

From this behavior we should expect the silicate of iron to hydrolyze more readily and to be completely decomposed at lower pH than the silicates of aluminum. Of this there is abundant evidence in nature. In the process of laterization, which undoubtedly is conditioned by a nearly neutral or alkaline reaction, the ferric oxide is the first of the amphoteric sesquioxides to be set free. Even in the colder humid regions where we meet with an acid reaction and where, for this reason, the higher silicates of aluminum should be stable, free ferric oxide is always in evidence as shown by the color of the red soils, the ferruginous clays and the brown forest soils of the temperate belt.

As far as the differences in the electrokinetic behavior between the aluminum and iron silicates and the differences we find between them under natural conditions are concerned we find, therefore, a complete general agreement.

THE SiO_2/R_2O_3 RATIO

The next question concerns the all-important relationship between the composition of the two series and the isoelectric pH. Does this relationship also express itself under natural conditions? To answer this question we must first inquire into the existence of regional differences (*a*) in the prevailing pH, (*b*) in the composition of the colloidal complex (for this purpose the composition of the most direct products of weathering as found in the parent material would seem to be more important than the composition of the soil colloidal complex which has been subjected to secondary changes characteristic of the soil body), and (*c*) in the composition of the drainage waters.

As to regional differences in the prevailing pH no systematic study has been made. But from reports on soil reactions in regions of heavy rainfall and in the absence of carbonates (the necessary conditions for our present study) it appears that the soil reaction in tropical regions where the conditions favor laterization is more nearly neutral whereas in the colder regions an acid reaction prevails. That this should be so can easily be explained. In the tropics, the weathering is much more intense. Quantities of strong bases are liberated by hydrolysis. The organic matter is rapidly oxidized into very weak carbonic acid and water. The reaction of the soil solution, especially when it reaches the lower zone of weathering on top of the parent rock, will remain neutral or even slightly alkaline in spite of heavy leaching. Under such conditions the hydroxides of aluminum and especially iron possess little or no power to bind silicic acid. The silicates undergo here a rapid alkaline hydrolysis (comp. fig. 26) the soluble products of which (the silica and the strong bases) will be leached out.

In the colder humid regions the weathering is much slower. Smaller quantities of strong bases are liberated within a given interval of time. The organic matter is transformed into acids much stronger than carbonic. The result is a more acid reaction. Under these conditions aluminum and, to a lesser

degree, iron will combine with silicic acid. The proportions of silicic acid thus fixed must increase within certain limits with increasing acidity, as shown in figure 27. [At low pH, aluminum and iron become ionically mobile as single and complex cations, that is, the complex undergoes an acid hydrolysis brought about by humic acids which displace the silica (13). This is pozolization which gives rise to a bleached layer of very high acidity and in which the remaining small amount of silicate complex should, and has been found to (1), possess a high proportion of silica. In the podzol B horizon the pH is higher. The aluminum and iron would therefore not be able to combine with as much silica as in the more acid A horizon but this is not the chief reason for the low ratio of silica to sesquioxides in the B horizon. The aluminum and iron exist here chiefly in combination with humic instead of silicic acid. The formation of this complex must therefore not be identified with laterization, as some would believe. The latter process consists of an alkaline hydrolysis, whereas podzolization is the result of an acid hydrolysis. The laterites possess little or no cation exchange capacity because they contain a low proportion of silica and practically no acid residue. The complex of the podzol B horizon may possess a considerable acid residue, due to humic acid, and accordingly a high cation exchange capacity.]

If now the reaction of the percolating water in humid regions changes from neutral in the tropics to acid in the colder zones we should anticipate an accompanying change in the composition of the products of weathering somewhat similar to the relationship shown in figure 27. On the one hand, i.e., in the tropics, we should expect the colloidal complex to possess a very low ratio of silica to sesquioxides, and on the other, i.e., in the podzolic regions of the North we should expect to find a more or less highly silicated colloidal material even where practically all of the strong bases have been lost through leaching. The intermediate zones would be expected to show an intermediate composition.

The meager data so far available support in a general way the predictions here made. The various publications of the Bureau of Soils workers (1, 7, 8, 20) represent the most valuable contributions to this subject. Byers and Anderson (3) have very recently published a general summary on the composition of the various soil colloids investigated in the bureau. From this work the writer has computed the average ratio of silica to sesquioxides in the soil colloids from the humid states of the Atlantic seaboard as far as represented. Table 92 gives this average for each state in the order of its latitude from Cuba to the St. Lawrence basin. The Cecil series are especially interesting because they occur on a wide stretch extending from Alabama to Virginia. We are therefore able to compute the composition ratio of the colloids from a single soil series as found in widely different latitudes.

The figures represent the average composition of the A, B, and C horizons. Whether this average composition ratio or the ratio in any one of the different horizons best represents the composition ratio characteristic of each locality cannot be decided. With the exception of the podzols the different horizons

do not differ greatly in composition. In the podzol B horizons the silica sesquioxide ratio is often very low because of the precipitation of "humates" of aluminum and iron. In such cases the ratio of silica to sesquioxides loses its significance. As already pointed out (15) the amphoteric behavior of the complex is a function of the ratio of the activity of the acid residue to the activity of the basic residue. In the podzol B horizons the SiO_2/R_2O_3 ratio may be very low whereas the ratio $\frac{\text{acid activity}}{\text{basic activity}}$ may be high. Any relationship between pH and composition must of necessity take account of all the acid and basic radicals present in the complex. To attempt this here would introduce complications beyond the scope of our present study. It should be pointed out, however, that the colloids from the Beckett horizons all contain a high humus content which undoubtedly has displaced silicic acid. This applies perhaps also to the Chester series, which are classified as gray-brown podzolic soils.

TABLE 92

The ratio of silica to sesquioxides in soil colloids from different latitudes of humid regions

COLLOID	LOCALITY	NUMBER OF ANALYSES	$\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$
Nipe	Cuba	3	0.30
Cecil	Alabama	3	1.27
Cecil	Georgia	9	1.33
Cecil	North Carolina	9	1.44
Davidson	North Carolina	4	1.44
Cecil	Virginia	3	1.60
Chester	Maryland	22	1.61
Leonardtown	Maryland	12	2.01
Podzols:			
Beckett	Massachusetts	5	1.74
Emmet	Michigan	3	2.93
Superior	Wisconsin	4	2.94

The table shows a definite, if not very great, increase in the composition ratio of the red Cecil colloids from Alabama to Virginia. The differences become very great as we examine the two extremes, i.e., the brick red Nipe laterite and the podzol colloids. Great local variations will undoubtedly be found. Such variations may be due to several causes affecting the prevailing pH. Thus the pH may be lowered by the oxidation of pyrites etc., or it may be increased by infiltration of waters from lime deposits. Variations in the humus cover and in the drainage are other factors. The nature of the vegetation is another factor which greatly affects the pH and the process of weathering.

A very interesting example of this latter influence has been brought out by Lundblad in Sweden (9), who points out that the brown forest soils of southern Sweden undergo a rapid "degradation" or podzolization in cases where the native hardwoods (beech) are succeeded by conifers (Norway spruce).

The relatively high pH under the hardwoods has given rise to a complex which possesses a comparatively low ratio of silica to sesquioxides. Under the more acid conditions following the growth of spruce this complex is no longer stable. Its isoelectric point is too high for the new environment and this leads to an acid hydrolysis resulting in a new complex with a higher ratio, which alone is stable at the lower pH.

THE $\frac{SiO_2}{MO + M_2O}$ RATIO IN COLLOIDS AND IN RIVER WATER

If the processes of weathering follow the laws of isoelectric precipitation we should expect to find evidence of this in the composition of drainage waters. The composition of the water which carries away all dissolved materials should be complementary to the composition of the insoluble residue—the colloidal complex. The composition of the water should even prove a surer index than the composition of soil samples, provided the waters to be compared represent humid regions which differ chiefly in the position of latitude.

The composition of soil colloids may vary greatly as a result of local conditions. The material may be recently formed or it may be very old, and formed under different conditions. Then we never know to what extent the colloidal fraction as separated by the super-centrifuge consists of unweathered particles of the original minerals. Glacial "rock flour" may yield colloidal material of this type. The composition of the drainage water must, on the other hand, constitute a most direct expression of what is taking place within the zone of weathering at the present time and represent the most complete general average obtainable.

In this connection our problem is simplified by the fact that we are not concerned with absolute values but merely with a ratio between certain constituents. It is clear that if the increase in the silica/sesquioxide ratio of soil colloids as we go from the tropics to colder regions is the result of a greater power of aluminum and iron hydroxides to combine with silicic acid as the pH decreases northward, then we should find a greater relative proportion of silica to the strong bases in tropical waters than in the waters of colder regions. The strong bases, especially Ca and Na, are rapidly lost as the minerals hydrolyze under humid conditions. Some of the silicic acid is, anionically, dispersed or dissolved together with the bases. How much of the silica which will thus pass into dispersion or solution will depend upon the extent to which the silicate ions are freed, by hydrolytic cleavage, from their union with Al and Fe and this will depend upon the pH.

Clarke (4) states that in natural waters "silica is actually present in the colloidal state and not in acid ions." Such distinctions are too sharply made. The colloidal state does not exclude ionization. A colloidal micella possesses all the characters of an ion and represents apparently an aggregate of ions and undissociated molecules. The degree of dispersion of the insoluble substance appears indeed to be closely related to the number of free ions (11). The ionization of the silicic acid will depend on the pH (comp. fig. 26) and will not

be wholly suppressed in the presence of, no matter how much, CO_2. It seems that too much emphasis is placed on the action of CO_2 in relation to the hydrolysis of silicate rocks. Theoretically we should expect a more rapid hydrolysis of silicates in a slightly alkaline than in a slightly acid solution since these materials are isoelectric on the acid side or, in other words, since the acid radicals are stronger than the basic radicals.

From data supplied by Clarke (4), and representing an average of about 1,700 analyses, the following figures on the composition of the igneous rocks have been computed. They express the percentage as well as the relative number of mols of four of the strong bases and of silica. Putting CaO = 1 we find:

	CaO	MgO	K_2O	Na_2O	SiO_2
Per cent	4.83	3.74	3.05	3.37	59.83
Mol ratio	1.0	1.08	0.37	0.63	11.48

This makes a ratio of $\frac{SiO_2}{MO + M_2O} = 3.73$

The corresponding figures for 44 of the soil colloids from various parts of the United States as reported by Robinson and Holmes (20) are as follows. (The Houston colloid is here omitted because of its $CaCO_3$ content):

	CaO	MgO	K_2O	Na_2O	SiO_2
Per cent	0.96	1.72	1.43	0.38	43.35
Mol ratio	1.0	2.50	0.89	0.35	41.90

The ratio of silica to the sum of the bases becomes in this case $\frac{SiO_2}{MO + M_2O} =$ 8.85

It is evident by comparing the two series of values that the bases are leached out in relatively greater quantities than the silica. The loss appears to be in the following order:

$$Na > Ca > Mg > K > SiO_2$$

The soil colloids studied by Robinson and Holmes represent soils of all degrees of maturity. If we compute the same ratio for the colloids of highly mature soils, such as the Cecil series, we obtain a different picture. The following figures are calculated from the 33 analyses of Cecil colloids as reported by Holmes and Edgington (8). These samples include the 24 whose silica/sesquioxide ratio is given in table 92. The authors give the pH values of the original soils. These values are also given in table 93. We shall find it instructive to give the average values for each state represented as well as the average values for the entire series.

In comparing the highly matured Cecil colloid with the colloids from various parts of the United States we note that: (*a*) All percentages of silica and strong bases have become lower but the loss of bases is by far greater than that of

silica. (*b*) All ratios have become wider. To 1 mol of CaO there are here 2.76 mols MgO, 1.67 mols K_2O, and only 0.33 mols of Na_2O, whereas the SiO_2 has increased (relatively) to 34.8 mols per mol of strong base. (*c*) In the different states the ratio of silica to strong bases increases as we go southward. (*d*) The pH of the original soils increases likewise in the same direction.

Before discussing these points we shall present, for comparison, the composition of river water from different regions.

The following ratios have been computed from the composition of river water, as given by Clarke (4). The rivers selected include those of the St. Lawrence Basin, of the Atlantic slope from Maine to Georgia, and of British Guiana. This represents a fairly continuous humid belt extending from the far North to the equator. The rivers have been placed into the same groups as given in Clarke's tables. The average values for each group were then calculated.

TABLE 93

The ratio of silica to strong bases in the Cecil soil colloids

LOCALITY	NUMBER OF SAMPLES	CaO	MgO	K_2O	Na_2O	SiO_2	$\frac{SiO_2}{MO + M_2O}$	pH
		per cent	*per cent*	*per cent*	*per cent*	*per cent*		
Virginia	3	0.08	0.62	0.56	0.07	39.41	27.2	4.53
North Carolina	10	0.18	0.33	0.51	0.05	36.52	34.2	4.90
Georgia	17	0.18	0.30	0.46	0.06	35.77	35.6	5.02
Alabama	3	0.13	0.23	0.32	0.09	35.17	45.6	5.23
General average:								
Per cent	..	0.17	0.33	0.47	0.06	36.30	.....	....
Mol ratio	..	....	....	....	....	.....	.....	....
CaO = 1	..	1.0	2.76	1.67	0.33	200.0	34.80	....

The composition of many of the waters represents the mean of a great number of analyses. The division is made into the following groups which include the lakes and rivers named:

I. St. Lawrence basin.
   Lakes: Superior, Michigan, Huron, Erie, Champlain.
   Rivers: St. Lawrence, Pigeon, Grand, Kalamazoo, Maumee, Genesee, Oswegatchie, Ottawa.

II. Maine to Pennsylvania.
   Lakes: Moosehead, Rangeley.
   Rivers: Androscoggin, Merrimac, Hudson, Raritan, Delaware, Susquehanna.

III. Maryland to North Carolina.
   Rivers: Potomac, Shenandoah, James, Don, Roanoke, Neuse.

IV. North Carolina to Georgia.
   Rivers: Cape Fear, Peedee, Saluda, Wateree, Savannah, Ocmulgee, Oconee.

V. British Guiana.
   Rivers: Barima, Waine, Essequibo, Demerara, Courantyne, Potaro.

For details the reader is referred to Clarke (4, p. 68).

It is very significant that the ratio of silica to strong bases increases rapidly as we go south from the St. Lawrence to the equator. The increase is from 0.19 to 1.55, or about 8 times in the latter region as compared to the former. Our object now will be to account for these observations.

If isoelectric weathering is a fact, if the laws of isoelectric precipitation govern the processes in nature as they do in the beakers of the laboratory, we shall have no difficulty in accounting for what we have observed because there is nothing which the theory does not demand. Everything that we have observed might, in a general way, have been predicted.

Let us first consider the interesting relationship between the pH, the composition, and the locality of the Cecil series of colloids (table 93). If the pH, as found, represents the prevailing, or at least the order of the prevailing, pH then we should expect the silica content of the colloid to be highest in the north

TABLE 94

The ratio of silica to strong bases in river waters of different latitudes

LOCALITY OF RIVERS	MOL RATIO. CaO = 1.0:					$\frac{SiO_2}{MO + M_2O}$
	CaO	MgO	K_2O	Na_2O	SiO_2	
St. Lawrence basin	1.00	0.45	0.03	0.17	0.31	0.19
Maine to Pennsylvania	1.00	0.34	0.07	0.49	0.55	0.29
Maryland to North Carolina	1.00	0.39	0.04	0.35	0.84	0.48
North Carolina to Georgia	1.00	0.35	0.13	0.92	2.10	0.88
British Guiana	1.00	0.99	0.15	1.90	6.28	1.55
For comparison we write again the same ratios for:						
Igneous rocks	1.00	1.08	0.37	0.63	11.48	3.73
44 soil colloids	1.00	2.50	0.89	0.35	41.90	8.85
Cecil colloids	1.00	2.76	1.67	0.33	200.00	34.80

where the pH is lowest (comp. fig. 27). Where the pH is higher the aluminum and iron silicates become more highly hydrolyzed, i.e., the silicate ions are displaced by OH, resulting in a liberation, dispersion, and solution of silica. More silica is therefore lost by the complex in the southern states. This is, however, true only when the rainfall is heavy enough to remove the strong bases, especially the divalent Mg and Ca which themselves form slightly soluble compounds with silicic acid and which are powerful coagulants of negative colloids. In soils of arid and semi-arid regions and also in the case of young soils or deposits in humid regions there can be no relationship between pH and composition. The colloids in such soils have usually a high silica/sesquioxide ratio in spite of a high pH but then their content of strong bases is always high (20).

The relation between pH and composition of the Cecil colloid might seem paradoxical when we consider the ratio of silica to strong bases. The lower

this ratio, that is, the higher the proportion of strong bases, the lower is the pH (see table 93). Before the amphoteric nature of the complex and its relation to the ultimate pH had been revealed this phenomenom could not have been understood. The fact is that the highly leached Cecil colloid is nearing an equilibrium condition. Its pH is not far from its ultimate pH. The small amounts of bases still left make little difference. The pH is dominantly determined by the silica-sesquioxide ratio and must therefore be highest where this ratio is lowest. A sample of Cecil colloid having a $SiO_2/R_2O_3 = 1.34$ yielded, when electrodialyzed, a pH of 4.75. Its isoelectric point was somewhat lower (15). The Cecil colloids studied by Holmes and Edgington and cited in tables 92 and 93 were nearly unsaturated. The pH must therefore be highest where the SiO_2/R_2O_3 ratio is lowest. A colloid of the order of the Cecil might be almost unsaturated at, let us say, a pH of 5.0, whereas another colloid having a very much higher ratio might be 50 per cent or more saturated at the same pH (15).

It thus appears that although the ultimate equilibrium composition (probably never quite attained) is governed by the prevailing pH, the effect in turn becomes the cause in that the pH is regulated by the composition.

If we now turn to a study of the ratios between the individual strong bases in the colloids we note, as already pointed out, that these ratios widen as the leaching progresses, being widest in the highly weathered and matured Cecil colloids. As far as the bases are concerned this widening in the ratios between them must be ascribed to a difference in stability of the compounds formed with the alumino and ferric silicates. It is well known that whereas a large part of the Ca (sometimes all of it) exists in the exchangeable condition only a very small part of Mg and K in soil colloids are subject to displacement by neutral salt cations. Mg and K appear to predominate in the interior of the particles, perhaps because they fit better into the ionic lattice and into the formation of slightly dissociated compounds. Mg and K would therefore be locked up in the interior of the particle during its formation from the products of hydrolysis. On the surface of the particles the relative proportions of the different cations are more like the composition of the soil solution (or river water) if we are to judge by the proportion in which the cations are exchangeable (2).

The widening of the ratio between the strong bases reflects the relative stability of the compounds which these bases form with the colloidal complex. Since practically all the strong bases are ultimately lost this difference in stability cannot affect the ultimate product of isoelectric weathering. But where a high stability retards the loss of a base it will also retard the loss of silica and thus postpone the final equilibrium condition.

Regarding the widening in the ratio of silica to strong bases in the colloids as compared to the igneous rocks the explanation is, on the basis of our theory, quite obvious. Below their isoelectric pH the sesquioxides combine isoelectrically with a certain proportion of silica, the proportion depending upon the

pH (see fig. 27). At the isoelectric point the amphoteric complex combines neither with anions nor cations to any appreciable extent. Therefore if the system tends to become isoelectric it is clear that the observed widening in the ratio between silica and strong bases must result.

Besides this widening in the ratio of silica to strong bases in the colloids as compared to the igneous rocks we also note a widening in the same ratio as the silica/sesquioxide ratio decreases or as we go from the north to the south, as is seen in the case of the Cecil colloids in table 93. As the silica content of the colloid decreases southward the strong bases decrease at a still higher rate. This is due to a very rapid decline in the strength of the acid residue as the silica content decreases. It will be recalled that the base exchange capacity is not a linear function of the number of mols of silica (or acid radical in general) present in the complex but that this capacity increases or decreases much more rapidly than the corresponding increase or decrease in the silica content (14). This means that the greater the proportion of sesquioxide the smaller is the free silicate mol fraction or acid residue and the smaller, therefore, the base-combining capacity per mol silica. In the laterites the often not inconsiderable quantities of silica possess hardly any combining power. Hence the widening ratio of silica to strong bases.

If we now examine the ratios of silica to strong bases as found in the river water we note that the ratios are, in a general way, complementary to those found in the soil colloids. The ratios found in the igneous rocks occupy a middle position (see table 94).

In respect to these ratios it should be pointed out that the presence of lime and other similar deposits may greatly alter the "normal" ratio which would result from the weathering of igneous rocks in each of the different regions. There are, of course, many other factors which will affect the ratios, such as differences in composition of the igneous as well as the sedimentary rocks. The sodium in many of the rivers near the ocean represents to a large extent cyclic salt. The nature and magnitude of a multitude of such disturbing factors are too difficult to trace and will not here be further discussed.

The quantities of sesquioxides present in the river water of the various regions are small and fairly uniform, as far as reported, with the exception of the brown waters of British Guiana which contain in some instances rather large quantities of Fe_2O_3. This iron is believed to have nothing to do with the actual process of weathering but rather to represent a secondary product resulting from the action of humus on the lateritic complex in the South American swamps. No account is therefore taken of this fact. It should also be pointed out that the humus has nothing to do with the high silica content in these waters, for, as Clarke states (4), the silica is equally high in the small streams near their sources.

The most significant thing about the composition of the drainage waters of the different regions is the ratio of silica to strong bases. The increase in this ratio from the St. Lawrence basin to British Guiana at the equator is so great

that all local irregularities can well be ignored. The differences must be due directly or indirectly to the climate. If the differences are the result of an isoelectric weathering then they depend upon differences in the prevailing pH and this in turn depends upon the climate.

In the St. Lawrence basin the pH must be low. The sesquioxides combine, therefore, with a greater proportion of silica. There is, therefore, on the average, only 0.19 mols SiO_2 going into solution with each mol $MO + M_2O$. As we go southward the prevailing pH increases, the OH ions take more and more the place of the silicate ions in the alumino- and ferric-silicate complex. The result is that the ratio of silica to strong bases increases in the drainage waters.

At the equator the soil reaction becomes more nearly neutral. Under these conditions ferric hydroxide combines with little or no silica whereas aluminum hydroxide unites with some silica even in a slightly alkaline medium. Very much greater quantities of silica will therefore be dissolved out together with the strong bases. In the river waters of British Guiana the ratio of silica to strong bases reaches a value of 1.55. This is still less than half of the same ratio in the igneous rocks, which is 3.73, but the difference is not so great if account is taken of the fact that a large part of the silica in the rocks consists of highly insoluble quartz.

Laterization is undoubtedly the dominant form of weathering in British Guiana. This is evident not only from the high ratio of silica to strong bases but also from the ratios between the individual bases which have become more narrow and approach the ratios in the igneous rocks. (The high value of 1.90 for Na_2O may be ascribed to cyclic salt from the ocean.) The laterites, and also bauxite, may contain considerable quantities of SiO_2 but they are, perhaps without exception, notorious for their poverty in strong bases. The low percentage of bases in the laterites is due to an extremely weak acid residue. The widening in the ratio of silica to strong bases observed in the case of the Cecil colloids and referred to in the foregoing attains a maximum in the laterites. The latter retain hardly any of the strong bases. The result is that the ratio between the bases in the drainage water will be more nearly that of the igneous rocks.

In closing it might be pointed out that isoelectric weathering is a tendency rather than a fact. It must not be assumed that the products of hydrolysis necessarily unite to form an isoelectric complex at the very outset. The isoelectric complex must possess the maximum stability but it is not the only stable compound. Comparatively high stability may extend over a wide range on either side of the isoelectric point. In combination with slightly dissociating ions, e.g., with divalent cations, the electronegative soil complex possesses a high stability and may resist decomposition for a long time even at a pH far removed from the isoelectric point. There must, however, even then be a gradual, if slow, trend toward an isoelectric composition. If the bases are lost more rapidly than they are returned to the soil (by man or by vegetation) this trend will be much more clearly manifested.

The same tendency toward the formation of an isoelectric complex might exist in the organic colloids as well. From the laws governing the isoelectric precipitation of proteins by humic acids and by the sesquioxides, as established by the author (16), we might conceivably account for certain facts such as the high percentage of nitrogen in the organic matter of the B horizon together with many other similar observations. This problem is, however, more complicated and cannot be discussed before certain questions, now investigated, have been answered.

In the next paper it will be shown how different soils and how the materials from different soil horizons react amphoterically.

SUMMARY

If an insoluble weak base as represented by $B(OH)_3$ reacts with a weak acid, as represented by H_3A, to form an insoluble compound then we may have

(*a*) $HA\begin{matrix}B(OH)_2\\B(OH)_2\end{matrix}$

(*b*) $HA = BOH$

(*c*) $\begin{matrix}H_2A\\H_2A\end{matrix}\!\!>BOH$

or any intermediate combination.

These compounds contain acid and basic residues of varying strength and react amphoterically. Where the acid residue is weak, as in (*a*), the isoelectric pH will be high and where the acid residue is strong, as in (*c*), the isoelectric point will be at a low pH. This relation between the composition and the isoelectric pH, which has previously been experimentally verified, has been applied to a study of the process of weathering. It is in general true that amphoteric compounds are least dispersible, least soluble, and least ionized, and are therefore most stable at their isoelectric point. Therefore, under conditions of heavy leaching, the tendency would be for the formation of an isoelectric soil complex.

A study of the prevailing pH in different latitudes of humid regions, of the composition of soil colloids and of river water supports this theory of isoelectric weathering.

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